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A Release of Internal Original Research Documents

Authored
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Chemistry Vol XII

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5 SUBJECT

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Chemistry Vol XII

Dec 2015

Acid-Base Chemistry
&
Chemlab Simulations

Page 1

Dec 02 2015 The Lodge @ Santa Fe.

What we are doing is working on the calibration of TDS meters, & attempting to equate it the conductivity.

The direct solution to the problem is that we measured

$$\frac{1.0\text{ gms}}{200.5\text{ ml distilled } H_2O}.$$

$$\frac{1000\text{ mg}}{200.5\text{ ml}} = \frac{x}{1000\text{ ml}} \qquad x = 4987\text{ mg}$$

This means, therefore, that we should have a PPM of 4987 TDS @ 25°C

Question: Does TDS change w/ temperature or only conductivity?

Yes according to HM meter, the reading will indeed change w/ temperature.

Therefore our temp is 20.1 $\Delta T = 4.9^\circ$
So the adjustment factor is $1.02^{(4.9)} = 1.10$
(2% per 1°C)

Therefore we should the reading $\frac{4987}{1.10} = 4533$

We are measuring 4430.
Not bad, it could be a little higher.

General: Not Salt NaCl!

Conversion of µS to PPM & PPM to µS.

We are now measuring 4500.
This is fine. The meter adjustment is
no more sensitive than this.

To convert to µS we believe we should
multiply by approx

1 PPM ≅ 1.56 µS
1 µS = 0.64 PPM

well, we learn that

7000 µS ≅ 4480 PPM

for NaCl 1 PPM ≅ 2.0 µS

$$\frac{7000\ \mu S}{4480\ PPM} = \frac{x}{1\ PPM} \qquad x = 1.56\ \mu S.$$

Therefore our estimated conductivity is 7000 µS
or ~ 7.0 mS.

Now, if we use the reference table.
We have

.05% NaCl @ 25°C = 1014.9 µS

@ .05% NaCl solution @ 200.5 ml is .10025 gms.
But we have 1.0 gms.
Therefore we'll have a $\frac{1.0}{.10025} = 9.975(.05\%) = 0.50\%$
solution.

Therefore we expect our conductivity to be

$$\left(\frac{.50\%}{.05\%}\right) 1014.90\ \mu S = 10149\ \mu S = 10.149\ mS$$

vs 7.0 mS.
This is reasonably in range.

We see that we are not off as much as we think, because we are using salt NaCl and the conversion factor for that is <u>2 to 1</u>!

So w/ NaCl:

1 PPM ≅ 2.0 uS

Therefore 4480 PPM $\left(\frac{2.0\,uS}{1\,PPM}\right)$ = 8960 uS

or 8.96 mS or ≅ <u>9.0 mS</u>

Our expected conductivity from the reference table is

10.0 mS

We are <u>right on</u> range!

We have now learned that we should have a reasonably well calibrated salt solution & that we should be able to estimate it with our Chemlab simulator.

Let test it. 1 gm NaCl in 200.5 ml H_2O!
Estimate 9.5 mS Conductivity

And the answer from our Chemlab simulator is <u>10.1 mS</u> Excellent work.

NaCl Conductivity in mS $\simeq$ PPM_{TDS} (.002)

General Conductivity in mS = PPM_{TDS} (.00156)

	Now for filtered water.	vs	Original Hotel H_2O
pH	= 8.1		9.2
PPM_{TDS}	= 84		108

These represent about a 20% reduction in TDS. This gives us an idea how effective the water filters are.

And now back to distilled water:

pH = Reset to 7 but having a hard time holding it.
PPM_{TDS} = 001

Conductivity Reference Table
Molecular weight of substance some
are in error!
eg FeSO4 shows 15.94

It is ~~15.94~~ !! 151.91

Lets Consider a mix of HCl, FeSO4 & NaCl
for Conductivity

HCl is 850mS @ 19%

$19\% = \frac{190mg}{1000ml} = \frac{85mg}{500ml}$

ok, we solve the coefficient by ~~trial & error~~.

1. Construct the given solution

$19\% = \frac{190gms}{1000ml} = \frac{85gms}{500ml}$ MW = 36.46

So we have a $\frac{190}{36.46}$ = 5.21M Solution HCl

So
850mS ⇔ 5.21M HCl Solution
163.15 ⇔ 1 M

So
mS = 163.15M HCl Solution

Page 6 RMS = square root of the mean of the squares.

There is a very intriguing proposition.

This is very interesting.

To Construct a 1M solution of HCl you:

1. Add 500 ml of water
2. Add ½ mole of 1M HCl Solution or 36.46/2 = 18.23 ml of 1M HCl solution. The density is the same as water so 1 ml ≅ 1 gm.
3. Check your work w/ the conductivity meter.

$$mS = 163.15 \times \text{Molarity of HCl solution}$$

you got 160.1 w/ the meter. Very close

4. Check Chemical properties - it shows 1/2 mole HCl
5. You do not understand why the pH is 7.0??

To construct a 3 layer mixture:

~~118.6~~	MW	1M Solution/100 ml	mS
NaCl	58.44	5.84 gms	118.6 ✓
$FeSO_4$	151.91	15.19 gms	33.5 ✓
HCl	36.46	3.65 gms (ml)	163.15 ✓

Now mix into one vessel. mS = ~~104.48~~ 105.13

Proposed / measured

$$\left[\frac{118.6^2 + 33.5^2 + 163.15^2}{3}\right]^{1/2} = 118.0\ mS \text{ vs } \cancel{105}\ 105.13\ mS$$

This is very close.

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It does indeed seem like the conductivity of a mixture is equal to the RMS of the individual contributions.

We can see w/ the HCl to construct a solution we need to use

500 ml - 3.65

Let's try to get pH to show up.

We must somehow add the dissociation of acetic acid

$1.000 (C_2H_4O_2) \rightarrow 1.000 (C_2H_3O_2^-) + 1.000 (H^+)$

1.75E-5

$1.000 (H_2O) \rightarrow 1.000 (H^+) + 1.000 (OH^-)$

LHS = 18.015

Pase 8

Heat of Neutralization Chemical List

Water	Stock
H+	~~Stock~~ Reaction Product
OH-	Reaction Product
1M HCl	~~Reaction Product~~ Stock, Solution
Cl-	St Reaction.
1M NaOH	Stock Solution'
Na+	Reaction.
NaCl	Reaction.

HCl · is sufficient.
NaOH [illegible] would be good.

18.015 4 Reactions are shown.

Diss Ass. Water — $1(H_2O) \rightarrow 1(H^+) + 1(OH^-)$
HCl Dissociation
NaOH Diss
NaCl Reaction.

Reactants: Water
Products: Hydrogen Ion
Hydroxide Ion

Good news! We have succeeded in creating an acid dissociation reaction & having it measured with a pH meter. This is great.
dissociation

NaOH dissociation
Reactants NaOH
Products Sodium
Hydroxide

Some equilibreum Constants

		~~Kb~~ Ka
strong	HCl	1.3E6
strong	Nitric Acid	2.4E1
weak	Acetic Acid	1.74E-5

		Kb
strong	Sodium Hydroxide	6.3E-1
strong	Potessium Hydroxide	3.6E-1
weak	Ammonia	1.80E-5

Now, how does NaOH have a pH of 14 in the UDL example and no Kb is specified.

Well, actually we see that it is wrong and it actually is 13.73 when Kb is specified.

Ok, you are now @ the point where you can mix acids & bases, & create acids & bases both strong and weak. This means that you can set up titrations now.

Ok, I have now figured out that the dissociation of water as a reaction set up as a prerequisite, a requirement to have any subsequent acid or base dissociation.

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Monoprotic Acid - Base Development

For Titration Exploration, I have now succeeded in creating

1 strong acid	HCl
1 weak acid	Acetic Acid
1 Strong base	NaOH
1 Weak base	Ammonia.

We should be able to titrate to no end now.

Question: How to remove a chemical?
How to transfer partially?

Some kind of problem w/ HNO_3?

[redacted]

Polyprotic also needed.

Can we recalibrate pH meter?

Topics Covered:

1. MW of Volatile
2. Conductivity
3. Acid Base Titration

Let's do a titration calculation.

Lets due a titration Calculation.

Apparently the reaction involved in the first experiment.

Strong Acid, Strong Base $HCl + NaOH$

$HCl \rightarrow H^+ + \cancel{OH}\ Cl^-$

$NaOH \rightarrow \cancel{H}\ Na^+ + OH^-$

Therefore the products are $NaCl$ & H_2O

So

$1.0\ HCl + 1.0\ NaOH \rightarrow 1.0\ NaCl + 1.0\ H_2O$

We started with 35 ml HCl, assume Conc. is unknown.

Ratio of NaOH to HCl is 1.

Therefore

$$\frac{35\,ml}{1.0M\ NaOH} = \frac{35\,ml}{\cancel{1.0}\ XM\ HCl} = \frac{1}{1}$$

Therefore

$$35\,ml \cdot XM\ HCl = (1.0M\ NaOH)(35\,ml) \quad = 1$$

So

$$\frac{\cancel{35}\,ml\ XM\ HCl}{1.0M\ NaOH \cdot \cancel{35}\,ml} \quad = 1$$

$X = 1.0\ M\ HCl.$

There is no way to solve it. Apparently we can use the relation of equilibrium.

$$\frac{[NaCl]^{1}[H_2O]^{1}}{[HCl]^{x}[NaOH]^{1}} = ?$$

Lets try the Strong Acid, weak Base

HCl + Ammonia

$H_2O +$ ~~$HCl + NH_4OH \rightarrow H^+ + Cl^- + NH_3^- + H^+ + H^+ + OH^-$~~

$HCl + NH_4OH \rightarrow H^+ + Cl^- + NH_4^+ + OH^-$

(x) ~~1.0~~ $HCl + \overset{1.0}{} NH_4OH \rightarrow 1.0\, NH_4Cl + \overset{1.0}{} H_2O$ This part is OK.

So Ratio of $\frac{NH_4OH}{HC} = 1$

~~We stoo~~ We used 70 ml of NH_4OH = ~~35~~

?? ∴ ~~1 mol of NaOH =~~ 1M $\overset{NH_4OH}{\cancel{NaOH}} = \frac{35.05 gms}{1000 ml} = \frac{X}{70 ml}$ 2.4535 gms

you need work here

~~X~~ and $\frac{2.4535 gms}{35.05 gms} = 0.07$ moles

0.07 moles HCl = $.07\left(\frac{36.46 gms}{1000 ml}\right) =$

$C_aV_a = C_bV_b$.

.35M NH_4OH is used to titrate 50 ml of 0.275M HCl
What volume of the NH_4OH is required?

We have an example problem.

weak base — strong acid

$NH_4OH_{(aq)} + HCl_{(aq)} \rightarrow H_2O + NH_4Cl_{(aq)}$

unknown for us. → $C_aV_a = C_bV_b$

a = acid
b = base

$C_a = \frac{0.275 \text{ mol}}{\text{liter}}$ V_a = 50 ml of HCl = .05 liters

$C_a = \frac{C_b V_b}{V_a}$

V_a = 10 ml
V_b = 70 ml
C_b = 1.0M

$C_a = \frac{1.0 \cdot 70}{10} = 7M????$

This makes no sense. It should be 1M?

Something is very wrong here. It make perfect sense that it would take 7 time the volume of a weak base to neutralize a strong acid. The equation $C_aV_a = C_bV_b$ in no way captures the relationship.
If it was a strong acid it would make sense.

Equilibrium Constant HCl = 1.3E6
Ammonia = 1.80E-5

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A source says that a strong acid will react w/ a weak base to form an acidic solution.
This is not what happened.

I can see that determining concentration (or find pH) is not so straight forward with a strong acid - weak base titration.

Let's see if we can roughly titrate alka seltzer w/ lemon juice.

alka seltzer pH ≅ 7.6 TDS ≅ 2340

Lemon Juice Drops	pH		$r^2 = .66$
5	7.5		2420
25	7.5		2550
35	7.4		2440
45	7.3		2480
65	7.2		2450
85	7.1	mistake	2420
→ 105	~~5.9~~	6.9	~~2410~~ 2370
125	~~5.8~~	6.8	2360
145	~~5.6~~	6.6	2390
165	~~5.4~~	6.4	2310
185	~~5.3~~	6.3	2350
205	~~5.1~~	6.1	2330

Estimated equivalence pt pH = 6.5

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The equivalence point is called the steepest part of the graph.

So you have this right. Now what does the equivalence point mean & why is it not always = 7?

It appears that the more common scenario is to start w/ the weak base and then add the acid.
So let's do this:

$C_aV_a = C_bV_b$ want C_b

$C_b = \frac{C_aV_a}{V_b} = \frac{1.0(\overset{15}{\cancel{50}})}{\cancel{15}\,50} = \cancel{333}$???

$10\,ml(\overset{2M}{\cancel{2\,ml}}) = (5\,ml)(\overset{4M}{\cancel{4\,ml}})$

$(1M)(50\,ml) =$ $\frac{C_a}{V_a} = \frac{C_b}{V_b}$

50

No No No

$\underline{C_aV_b = C_bV_a}$

The reaction is

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

$NH_4OH + HCl \rightarrow NH_4^+ + OH^- + H^+ + Cl^-$

$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$

Dec 10 2015

German Database search

		Complex	Aerobic	SubMedia
pH 4.5	Acidulprofundum	T	T	F
	Much more convoluted, no iron			
	Hippea Jasoniae	T	T	F
	Much more involved $FeCl_3$			
	Caldisphaera	T	T	F
	Much more involved $FeCl_3$			

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Dec 11 2015 Friday.

We can streamline our set for now to:

1 1. Chemlab exploration on the netbook
1 2. Speedwriting is actually fun
3 3. German database later today
1 4. Voltammetry CV-27 manuals
2 5. Polar group article
2 6. Is citrate a buffer?
3 7. Webinar on papers?

So the Preferences are

Most desired: We also love our molecule book!

Chemlab simulations & chemistry study!
ok * We start! → Voltammetry CV-27 direct access!
ok We love! Speedwriting fun

Moderately desired:

Polar group article
Is Citrate a buffer - what is a buffer?

Least desired, but still desired!

German database
Webinar on papers

[redacted]

We start today by studying the CV-27 manual.

We have, in the CV-27 a current to voltage converter with a range of

2uA/Volt to 10mA/Volt.
in 12 steps.

We can supposedly accomplish!:

Amperometry
Chronoamperometry
Chronocoulometry
Cyclic Voltammetry
Linear Scan Voltammetry
Stripping Voltammetry
Controlled Potential Electrolysis
Potentiometry
Spectroelectrochemistry.

Wow! This is fantastic
Titration also mentioned.

There are two books that would be useful.

The leads are identified
Working electrode is black
Reference Electrode is white
Auxiliary electrode is red.

[redacted]

or Black - ~~Reference~~ Working
White - Reference
Red - Auxiliary

Make sure the cell mode is in STANDBY when turning the unit off or on!

The meter display can give us directly I out. Notice we also have Q that can show up: How?

The application of 1 or the other of two fixed potentials are numerous. Let's learn what they are.

The display outputs actual value in the appropriate units. The output jacks in the rear are affected by the gain current to voltage converter.

$\text{Gain Control} = \frac{mA}{V}$ so $V = \frac{mA}{\text{Gain}}$

or $mA = \overset{\text{known}}{V} \cdot \overset{\text{known}}{\text{Gain Control}}$

The HOLD button looks like it sets step to E_1 or it can be stepped to E_2 by switching to E_2

You should have no problem understanding I out now. I & voltage but only because of the converter.

E on the rear panel in the manual is actually ΔE and then is the equilibrium potential of the working electrode (black electrode) relative to the reference electrode (white).

Semi diff also looks to be very ~~interesting~~. The fiddles can apply here also.

We actually learned quite a lot here about the Controls.

Letts test the gain theory.

$AppE = 1.0V$

$Gain\ (mA/V) = 10$

We have $mA = V \cdot Gain\left(\frac{mA}{V}\right)$

So $mA = 1.0V \times \frac{10\,mA}{V} = 10mA$

but this again does not matter because the actual output from the test is 0.10 A or 100 mA

Once again we are led to the figure of 10 as a factor.

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We believe therefore, that the actual relationship is

$$I(mA) = (\text{App } E)(10) \cdot \text{Gain Factor}$$

and don't ask me why.
Example:

$$200\,mA = (1.0\,V)(10)\left(\frac{5\,mA}{V}\right) = 50\,mA$$ No! It is 200.

So the relationship is actually

$$I(\text{amps}) = \frac{\text{App}E(V)}{\text{Gain}\left(\frac{mA}{V}\right)}$$

or

$$I(\text{amps}) = \frac{\text{App}E(V)}{1} * \frac{1}{\text{Gain}(mA/V)}$$

or in MA

$$\boxed{I(mA) = \frac{1000 \cdot \text{App}E}{\text{Gain}(mA/V)}}$$

This should work.

This is not what the book has. they have the reciprocal

Example

$$\boxed{200\,mA = \frac{1000\,mV}{5(mA/V)} = 200\,mA}$$

this works

Notice the Semi Dry test can also be run.

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We also see that we should be able
to conduct other tests as well.
eg Coulometric test.

These tests would be of interest &
will expand your capabilities &
understanding of the instrument.

—

for
Cyclic
Voltammetry

It is interesting to me that $V = f(t)$
was again shown as the model template
but then it was flipped to $I = f(V)$

I truly do not see the reason or requirement
for this.

—

I am not sure that Chronoamperometry
is going to be that useful to us.
It steps between E_1 & E_2 directly.

It is used primarily for electrode area,
or diffusion coefficient, or electron
stoichiometry.

You could @ least try it, however.

—

Next is Chronocoulometry.
This is the integration of
Chronoamperometry.

Next:
Stripping Voltammetry does look interesting. It is very useful for trace metal determination

They is stated to use a mercury electrode, which we definitely do not have —

Rani p116 of Electroanalytical Methods is about Stripping Voltammetry.

Laksh Ch 6, p66 of Electronanalytical Techniques is all about Stripping Analysis

Iqbal p135 Textbook of Electrochemistry gives a summary overview of Stripping voltammetry.
It appears to be a summary only w/ no detail.

Rao p89 Electrochemistry for Environmental Protection has an entire chappter on Stripping Voltammetry.

Stripping voltametry is strongly tied into a mercury electrode. We do not have this and do not, as of now, anticipate having one.

It is a very sensitive technique.

I can see that conc. nitric acid will dissolve hair.
We need some.

500 ml of HNO_3 (65-70% conc)
will cost me $38
\+ 25
\+ reg shipping 15 This is a problem.
$78

Why do the electrodes need to be different for voltammetry?
You see that they do not always have to be.

Controlled Potential Electrolysis is next.

Fixed potential, integrated to produce Q.

Made for assays, instead of ~~trace~~ trace analysis. What exactly is an assay?

Next is Amperometry.
Fixed potential, measured current.
It plateaus. We should be able to do this. Useful for concentration w/standard curves.

It can also be used for titration and for detection in flow meters.

Next is Potentiometry.

Potential is measured under a condition of no current. This is an equilibrium process.
Used for the determination of

pH, Na^+, K^+ Ca^{2+}, Cl, F, CO_2, NH_3
& water hardness

Electron microphotographs, though minutely detailed, suffer from two failings. They cannot depict living subjects and they are invariably monochrome except those that are artificially colored afterwards.

Dec 12 2015 Saturday

It looks like we have the Chemlab Simulator fully functional on the NetBook now!

These folders need to be copied:

1. Chemlab in Docs
2. Model Science in Programs x 86
3. Chemlab in AppData / Roaming

This looks like it gives you everything. Very good.

Your titration experiment Dec 06 2015-01 Gives you a

1. Strong acid	HCl
2. Weak Acid	Acetic Acid
3. Strong Base	NaOH
4. Weak Base	Ammonia

Pipettes
a Burette
a Mixing Container

You also need the dissociation Constants

You have set this up to include the

1. Dissociation of H_2O
2. Dissociation of HCl
3. Dissociation of Acetic Acid
4. Dissociation of NaOH.
5. Dissociation of Ammonia

w/ Reactants & Products for Each one.

This is a powerful lab and it is how you discovered the meaning & properties of a buffer.

You have titrated but you still do not know how to determine concentration. This was a real weakness.

Rather than using Acetic Acid as your weak acid, it would be of interest to use Citric acid since you have it available.
It would be of even more interest to create a weak base & a weak acid - is that what makes a buffer or is it a weak acid & a strong base? What makes a buffer?
Citric Acid ?
Baking Soda?

p286 From Schaum, there is more than one way to create a buffer.
A weak acid & a strong base is indeed one method.
You really do need to study buffers & pH and concentrations.

Utterly Confused has good chapters: - Moore

4 Aqueous Solutions exp 4-3
15 Acids & Bases
16 Buffers

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We start by std solubility in Moore

Group 1A carbonates & phosphates are soluble.
Group 1A hydroxides are also soluble
Group 1A oxides are soluble
& Group IIA metaloxides react w/ water.

Barium hydroxide is stated to be a strong base but I did not think that it was V sly soluble.

Acids react w/ bases to produce H_2O & a salt.

Moore gives an example of titration w/ acetic acid (vinegar) w/ $Ca(OH)_2$
You need the balanced reaction to do anything.

$$2HC_2H_3O_2(aq) + Ca(OH)_2(aq) \rightarrow Ca(C_2H_3O_2)_2(aq) + 2H_2O$$

60.053 gms/mol

Lets see if Chemix Balances.
Maybe we should get one in Android?

OK Chemix Worked and Android worked ~~Ht~~ And Android misspelled the program!
but it works!

Chemix and Android Balancing both worked.

Chemical Predictor is now working on NetBook
= along w/ Chemix

And Equation Balancer is also working on android but you cannot split up elements w/in a compound.

So This is acetic acid

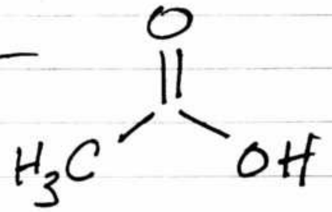
$C_2H_4O_2 + Ca(OH)_2 \rightarrow Ca(C_2H_3O_2)_2 + H_2O$

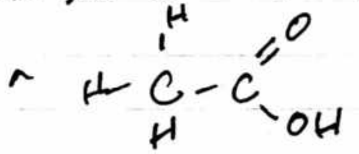
balances to

$2C_2H_4O_2 + Ca(OH)_2 \rightarrow Ca(C_2H_3O_2)_2 + 2H_2O$

w/ 2 separate android programs & Chemix on Netbook!

Acetic acid is also written as $HC_2H_3O_2$
Let's see what it looks like.





So acetic acid is a methyl group attached to a COOH group. Can't get more basic than that. Definitely an organic acid.

Now that we have a balanced equation we can begin to approach titration questions.

Given 0.250 mole of acetic acid.

Question: How many moles of $Ca(OH)_2$ are required to titrate the acetic acid?

We know that the ratio of acetic acid to Calcium hydroxide is 2 to 1. Therefore we need 0.125 moles of $Ca(OH)_2$.

and this is correct. Now to titrate means that we are bringing the pH to 7.0.

Now, the next problem gives us liters instead of moles, so!

Given 0.05 liters of a 0.100 moles of acetic acid.

We know that 0.05 mole of $Ca(OH)_2$ are required if a full liter is involved.
But a full liter is NOT INOLVED.
There is only 0.05 liters involved.
So the actual answer is:

$$0.05 \text{ liters} \left(\frac{0.05 \text{ moles}}{\text{liter}} \right) = 2.5E{-3} \text{ moles.}$$

So remember that M in solution means $\frac{\text{mole}}{\text{per liter}}$ not just moles.

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Now he is moving on to another variation.

Given 0.2 mol acetic acid.
Question: How many gms of $Ca(OH)_2$ to titrate?

So if we have 0.2 mol acetic acid, then 0.1 mol of $Ca(OH)_2$ are required to titrate.

1 mol of $Ca(OH)_2$ = ~~58.09~~ gms/mol Wrong

so 0.1 mol = ~~5.8~~ gms Wrong

But he has a molar mass of 74.10 gms/mol
Why this difference?

Answer is 74.09 gms/mol Chemical Suite worked

Ca	40.08	40.08
O	15.99	31.98
H	1.01	2.02
		Σ = 74.08

* Do not use Chemistry Toolbox for Molecular Mass. Use Chemical Suite instead.

0.1 (74.08) = 7.41 gms ✓ OK

Chemistry Toolbox has a PROBLEM!
Sent email.

Now we go on to even another variation.

Given: .025l of $Ca(OH_2)$ was necessary to titrate 0.04l of a 0.1M acetic acid.

Question: What is the Conc. of the ~~$Ca(OH_2)$~~ $Ca(OH)_2$ solution?

Method:

If we have a 0.1M Acetic Acid solution we have $0.1 \frac{mol}{liter} \left(60.053 \frac{gms}{mol}\right) = 6.01 \frac{gms}{liter}$

acetic acid.

So our solution is a 0.1M solution of acetic acid.

We know that it takes a .05 M solution to titrate it if volumes were equal.

But they are not equal.

We have $\frac{.025l}{.04l} = .625$ as much.

So it is <u>more</u> concentrated.

So the concentration is $\frac{6.01 \frac{gms}{liter}}{.625} = 9.616 \frac{gms}{liter}$

and since $Ca(OH)_2$ has a MW of $74.08 \frac{gms}{mol}$

$\frac{9.616gms}{74.08gms} = \underline{0.13M}\ Ca(OH)_2$

The answer is 0.08M

So we are wrong.

So isn't it true that

$$C_a V_a = C_b V_b$$

but does this account for molarity?
Wouldn't it be

$$M_a C_a V_a \overset{?}{=} M_b C_b V_b \quad ??$$

We need C_b

$$C_b = \frac{M_a C_a V_a}{M_b V_b} = \frac{1.0(0.1)(40\,ml)}{0.5(25\,ml)}$$

$C_b = 0.32\ M$ Nope !!!

This does not work either. !!!

So lets see why are we so confused about this? It seems like there is more than one way of going about things w/ different equations involved & then factor is all rather confusing.

So the answer is to practice practice practice until you get it get it get it.

So let's go through her reasoning process first & compare it to lots of my attempts that obviously failed.

Moore's Method p59

Given

0.025 l $Ca(OH)_2$ were required to titrate 0.04 l of a $0.10M$ (actually $\frac{\text{moles}}{\text{liter}}$) acetic acid solution.

Question: What is the conc. of the $Ca(OH)_2$ solution?

We know that:

$$2\,C_2H_4O_2 + Ca(OH)_2 \Rightarrow Ca(C_2H_3O_2) + 2H_2O$$

To titrate 0.04l of a $0.10M$ acetic acid we need of $Ca(OH_2)$ =

$$.04\,l\left(\frac{.10M}{\text{liter}}\right)(0.5) = 2E\text{-}3\,\frac{\text{Moles}}{\cancel{\text{liter}}}$$

$$\frac{2E\text{-}3\,\text{moles}}{.025\,\text{liters}} = \frac{X}{1\,\text{liter}} \qquad X = 0.08M\ Ca(OH)_2$$

So this looks reasonably straightforward in thinking.

1. We know the relationship of moles of reactants
2. We can determine the actual moles per specified volume of reactant
3. We use the definition of molarity to arrive @ the molar/concentration of the other reactant
4. When you think of a M solution, you want to remember it actually means moles/per liter

The problem was actually a lot of fun
when you think about it.
It is exactly the type of problem that
we are doing in the ChemLab simulator.

We are:
1. Having a certain volume of a weak acid, of a ~~certain~~ unknown conc., for example
2. We titrate it w/ a known concentration of
   a strong base.
3. We should therefore be able to determine the
   conc. of the weak base.

You must know the chemical reaction before
you can proceed.

We are working with acetic acid & NaOH

$$C_2H_4O_2 + NaOH \rightarrow H^+ + C_2H_3O_2^-$$

$$+ Na^+ + OH^-$$

so

$$\text{or} \rightarrow NaC_2H_3O_2 + H_2O$$

sodium acetate

$$C_2H_4O_2 + NaOH \rightarrow NaC_2H_3O_2 + H_2O$$

It is already balanced!

We can now try this in the simulator.

Now we are in the simulation.

Let assume we add 100 ml of acetic acid
and assume that we do not know the
concentration of it.

Titrate it w/ 1.0M NaOH
&
Use the reaction
$C_2H_4O_2 + NaOH \rightarrow NaC_2H_3O_2 + H_2O$

to determine the concentration of the acetic acid.

We did not have a molarity for the acetic
acid, so how would you know what you have.
We have changed it to 1.0M acetic acid.

Given 100 ml unknown acetic acid (actually 1.0M)
Now titrate
Starting volume: 15.00 ml

You have a problem. The acetic acid is no
longer an acid

Acetic Acid Dissociation is 1.74E-05
Ok, we have reset the dissociation reaction
of acetic acid w/ 1M solution

Ok, we now have 100ml of acetic acid of unknown concentration (actually we know that it is 1M) w/a pH of 2.38.

Before we did not have the concentration of acetic acid specified, so who knows what we'll find.

Now lets titrate. w/NaOH (1M)

You need to 3 Steps:

1. open titration dialog box
2. Collect titration data
3. View titration data

Starting volume 15ml.

So it only took about 2 ml of 1M NaOH. We can see from the raw data that it flipped over @ 2.15ml of NaOH.

Is this enough to solve the problem? Lets try it.

Given: 2.15 ml of 1.0M NaOH titrates 100 ml of acetic acid.

Question: What is the concentration of the acetic acid.

The mole ratio is 1 to 1.

~~[illegible]~~ NaOH = $\frac{1 \text{ Mole}}{1 \text{ liter}} * .00215 l = .00215$ moles NaOH

We know that it ~~produces~~ requires $\frac{.00215 \text{ moles acetic acid}}{\text{in } 100 \text{ ml of acetic acid}} = \frac{.0215 \text{ M acetic acid.}}{1000 \text{ ml}}$

Did not work. Why?

[redacted]

Lets try again:

Given 500 ml of unknown conc. of acetic acid. (pH = 2.38)

Now titrate. 35ml 1.0M NaOH

It took 45.35 ml to neutralize.

So 45.35ml $\frac{1 \text{ Mole}}{1000 \text{ ml}}$ = .0454 moles NaOH required.

We know therefore that .0454 moles of acetic acid were required.

0.09 M acetic acid.

$\frac{.0454 \text{ moles}}{500 \text{ ml}} = \frac{\cancel{0.9 \text{ M}}}{1000 \text{ ml}}$

This does not work either. Why???

We have a dissociation constant for NaOH of 0.63
is this correct?
It seems to be right. How could we be so far off then?

Seems like screwy results.
Why?
Let repeat this one.

Again:

500ml unknown acetic acid (actually 1.0M)

You get exactly the same result @ 45.35 ml NaOH 1M

So I am not sure what is wrong
Let's change acetic acid to 0.5M
And see if it take half as much.

Now using 500 ml unknown acetic acid (actually 0.5M)
pH is 2.53

Incidentally it says it has 0.248 moles in solution

We get 22.15 ml   This is indeed very close to 1/2.

I wonder why this is not working?
It is consistent, but it seems wrong.

Action Plan

Now that you know how the problem should works, you can use the control simulation to ~~test~~ the process and then look for differences.

Dec 15, 2015 Tuesday
@ Three Rivers

Let's go to Chemlab strong acid strong base

We have 35ml of 0.2M HCl
We added a pH meter and we have 0.7

One of your problems is to learn how to determine pH of a certain concentration.

Now, before we get too involved here let's look @ the reaction

$HCl \rightarrow H^+ + Cl^-$
$NaOH \rightarrow Na^+ + OH^-$

$HCl + NaOH \rightarrow NaCl + H_2O$
It is balanced so 1.0M HCl combines w/ 1 mol NaOH.
Let's titrate.
* The pH of the 0.2M NaOH is 13.30.
Ok, we have done it.
It takes exactly 35 ml NaOH 0.2 M to reach the equivalence point.
How do you know that 35 ml is 1 mol since the MW's are different?

Let's work that thing.

Equivalence is reached @ exactly 35.00 ml.

Given

35 ml of an unknown concentration of HCl.
(Actually we know that it is 0.2 M)

It takes 35 ml of 0.2 M NaOH to neutralize the HCl.

Question: What is the concentration of the HCl?

$35\,ml\left(\frac{0.2M}{1000\,ml}\right)$ = 7E-3 Moles of ~~HCl~~ NaOH were used.

We know, from the balanced equation, that 7E-3 moles of ~~NaOH~~ HCl are required..
~~We know that 35 ml of NaOH were required~~.
What is the concentration of the HCl?

Concentration = no. ~~of moles /~~ ~~* Volume~~ in ml / ~~Volume 1000~~ ml

but this is more intuitive

$\frac{7E\text{-}3\,moles}{35\,ml} = \frac{x}{1000}$

$x = 1000\,ml \cdot \frac{7E\text{-}3\,moles}{35\,ml} = 0.2M$

This means the concentration of the HCl is 0.2M
which is correct.

No. of moles in given solution * 1000 ml = Molar Concentration * Partial Volume

or Molar Concentration = $\frac{\text{No. of moles in given Solution} * 1000\,ml}{\text{Partial Volume in ml}}$

g Molar-Concentration = $\frac{7E\text{-}3\,(1000\,ml)}{35\,ml}$
= 0.2

This indeed works

Now, let see if we can create our own '~~Salt~~ lab.

Need dissociation for HCl & NaOH.
1.3E6 6.3E-1

So if they have different dissociation constants how can they use equal volume to titrate?

—

We are now trying to create our own lab.

We have successfully created HCl @ 0.2M w/ a pH of 0.70, the same as the default lab.

This is great. I have also succeeded in setting up the 0.2M NaOH and the pH is 13.20 which agrees very well with the default lab @ 13.30.
So it appears that we have successfully replicated the default lab.

Let test it w/ a simulated titration.

The titration has worked! Very good Clifford.

Now think about titration. What does it really mean? The formation of salt & water — does it occur only @ the equivalence point? It would seem as though this is the case.

Because when you keep adding NaOH you flip the pH to 12.5+, which is hardly neutral so it can hardly be 'salt + water'.

I wonder how you express the creation of salt & water in Chemlab?

We are actually flipping now @ 33.35 ml vs 35.00 not sure what is causing that difference.

Lets try a titration w/ an offset in concentration
ie HCl @ 0.3M and NaOH @ 0.15M.

Ok, we changed the pH of HCl to 0.52 when we changed the molar concentration to 0.3 vs pH of 0.70 @ molar concentration of 0.2

Also the pH of NaOH has changed to 13.10 instead of 13.20 or 13.30 as it was when the molar concentration was 0.2. Now it is 0.15 so the pH is less. Obviously you would have to learn how to determine the pH of an acid or base as a function of concentration.

Now lets titrate 35 ml of 0.3M HCl with 0.15M NaOH and assume we do not know the concentration of HCl.

You think that it will take 10 ml.

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We now have 2 main questions:

1. What happens when you use a strong acid weak base combination, or visa versa. Why did my earlier experiment fail? Use a default to learn from.

2. How do you determine the ~~concentration~~ pH of an acid or base based upon its concentration?

Let's go to mixed strength problem.

Strong Acid - Weak Base Titration Default Case.

The reactions are	MY TRIAL So you see that you have a handful.
1. Diss of Acetic Acid	✓
2. Diss. of HCl	✓
3. Diss of NaOH	✓
4. Na & Cl reaction	You did not include this
5. Hydrolysis of acetate	You did not include this
6. Diss of Water.	✓
	Diss of Ammonia

Therefore, you may have missed two very important reactions. Let's go back to the ChemLab default. ~~Do~~ The Chemicals Are:

H^+
OH^-
0.1M HCl
Cl^-
0.1M $NaOH$
Na^+

$NaCl$
0.1 $C_2H_4O_2$ (Acetic Acid)
$C_2H_3O_2^-$ (acetate ion)
$NaC_2H_3O_2$ (sodium acetate)

MY TRIAL:

H_2O
H^+
Cl^-
1.0M HCl
$C_2H_3O_2^-$
0.5M $C_2H_4O_2$

OH^-
1.0M $NaOH$
Na^+
OH^-
1.0M NH_4OH
NH_4^+

[redacted]

What we need to do:

Determine the Conc. of the unknown acid or base based upon Chemlab default lab.

When this is correct, we then verify we can duplicate the lab w/ our own file.

We will skip the strong acid - strong base reaction since we have this one under control.

We will work w/ titration of a weak acid w/ a strong base.

Notice our pH of the 0.1M Acetic Acid is 2.88.

In our standard lab of weak acid - strong base we see some important things right away.

First we see that the mid point of the steep curve is NOT @ 7.0. This is undoubtedly important.

Our lab results are

notice Given: 30ml of 0.1 $C_2H_4O_2$

notice Titration result: 30ml of 0.1M NaOH reaches equilibrium @ pH ~ 88.

CH_3COOH is a great way of recalling acetic acid!
A methyl group attached to a COOH group.

Moore is discussing $CH_3COOH + NH_3 \rightarrow CH_3COO^- + NH_4^+$
Acetic Acid   Ammonia

Now ChemLab is saying, for ~~HCl dissociation~~ example CH_3COOH

$HX \Rightarrow H^+ + X^-$ and X^- is the conjugate base
So in our case the acetate ion should be the conjugate base.
Now we have an ~~el~~ equilibrium constant

$$Ka = \frac{[H^+][X^-]}{[HX]}$$

Now, how do you actually apply this?

Let's apply this to something. Notice also the volume are still equal when .1M NaOH & .1M CH_3COOH are used. Is it because both are .1 and 1.0M is for both reactants? This is a curious affair. This is obviously where

$C_aV_a = C_bV_b$ Comes from

Is this true for weak acid strong base combination as well?

I think that you need to study Moore.

Conjugate acid-base pairs differ by only a single H^+.

Now we understand this because of

$$HX \rightarrow H^+ + AX^-$$

Notice that it hardly has to have a COOH group for x but it certainly does not have to, take HCl for example.

Notice double arrows vs single arrows in reactions.

H^+ is the same as H_3O^+

Water itself dissociates. This can be written either

$$H_2O \leftrightarrows H^+ + OH^-$$

or

$$2H_2O \rightleftarrows H_3O^+ + OH^-$$

$pH = -\log[H^+]$ or $\underline{\text{equivalently}}$ $pH = -\log[H_3O^+]$

The equilibrium expression for water is

$$K_W = [H^+][OH] = 1E-14$$

in water $[H^+] = [OH^-]$ so

$$[x]^2 = 1E-14$$

$x = 1E-7$ $\quad$ $pH = -\log[1E-7] = 7$

[redacted]

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and this is *not* the same as the natural log, ln.
Temperature is an important variable for both equilibrium & pH.

Here comes our method to determine pH of a particular concentration. This is great

Determine pH of .025M Nitric Acid!

$$\overset{.025}{HNO_3} \rightarrow \overset{.025}{H^+} + \overset{.025}{NO_3^-}$$

K_a = · We did not use or need this!

We know that it completely dissociates. So we simply said

$$pH(\overset{.025M}{HNO_3}) = -\log[.025] = \underline{\underline{1.60}}$$ This is it.

Water does not enter into the problem since the concentration of water H^+ is so low.

So all that you needed to know was the fact that the acid completely dissociates and the molar concentration. That is pretty amazing. So we can already use this in Chemlab for strong acids & bases.

We could test them already but it would be better to get involved w/ weak acids & bases first.

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Now going backwards.
A solution had a pH of 8.75

What is the concentration of ~~OH~~ H^+ & OH^-

$pH = -\log[H^+]$ or $\log[H^+] = -pH$

$H^+ = 10^{-pH}$
$H^+ = 10^{-8.75}$
$H^+ = 1.8E-9$ OK✓

Now $pOH = 5.25$

$OH = 10^{-5.25} = 5.6E-6$ OK✓

Now, doesn't this assume that
1M H^+ and 1M OH^- are created
in the reaction.

Ok, good. But now we get to Ka & Kb
which is what we really want now.

Ke in general is called an equilibrium
constant.

but Ka is more specifically an acid
dissociation constant [It is
actually also an "equilibrium constant"!!

The equilibrium constant Ka is

$$Ka = \frac{[H^+][A^-]}{[HA]}$$

from $HA \rightarrow H^+ + A^-$

If we actually recall that it really is

$$HA + H_2O \rightarrow H^+ + A^-$$

we see that the water is not incorporated into the equilibrium expression and is regarded as a constant.

Moore does not give a table of dissociation constants, let's try to find a table.
I have a table now of bluefire
for the weak acids & bases.
No strong acids or bases in her table.

strong	H_2SO_4	1.2E-2	
We have		Ka	
strong	HCl	1.3E6	
strong	Nitric Acid	2.4E1	
weak	Acetic Acid	1.74E-5	CH_3COOH
		Kb	
strong	NaOH	6.3E-1	
strong	KOH	3.6E-1	
weak	Ammonia	1.80E-5	

[redacted]

If we know molarity & K_a, we can calculate

H^+ or A^- (and this means pH!)

We obviously need to do this rather than just say that we can.

Also, you know the molarity of a base and K_b we can calculate

OH^- or HB^+ (and this means pOH!)

And we need to show this rather than just say that we can do it.

We can test this w/ ChemLab!

After this I also want to learn the algebra from the proof at Eugene Oregon.

[redacted]

[redacted]

This is also interesting:

$Ka \cdot Kb = Kw$.

So the product of conjugate acid - base pairs always equals that of water 1E-14

Now here is an interesting statement.

Salts & Oxides have acid base properties.

So to understand this, it seems like you should work with the Lewis definition of an acid & base

Lewis acid accepts a <u>pair</u> of electrons

Lewis base donates a pair of electrons.

Now Moore does not introduce Lewis when he talks about oxides and salts. His rationale for oxides is as follows:

It is because they react with water to form a base. (This is certainly not the case with Fe^{+2}!)

Example $Na_2O + H_2O \rightarrow 2\,NaOH$

(sodium Oxide)

So why is Fe^{+2} so acidic.

Well, we have certainly found an explanation source, and Fe^{+3} is even more acidic than Fe^{+2}. It is the coordination complex with water that causes it.

Given 0.3M Acetic Acid
$K_a = 1.8E-5$

What is H^+, ie what is pH?

CH_3COOH

$C_2H_4O_2 \rightarrow H^+ + C_2H_3O_2^-$

Seems to me that we could assume in a H_2O solution a that effect of H_2O is negligible

Seems to me that we should have

$$\left[\underset{H^+}{.3M}\right]\left[.3M\ C_2H_3O_2\right] = 1.8E-5$$

or $.3^2x^2 = 1.8E-5 \quad x = .014$

and $pH = -\log[.014] = 1.85$

And we are wrong.

It should be framed as

$$\frac{[H^+][C_2H_3O_2^-]}{[C_2H_4O_2]} = 1.8E-5$$

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We Can progress the forward t.

$$\frac{[H^+][C_2H_3O_2^-]}{0.3}$$ (disregarding water influence)

Now, I thought that H^+ was 0.3 M and same for $C_2H_3O_2^-$ but
THIS IS NOT TRUE!

He calls it X.
This means he does not know the Concentration of H^+ and $C_2H_3O_2^-$ that are produced.
You will need to explore equilibrium expression & stoichiometry more thoroughly to understand the origin of the little.
So assuming therefore that it IS "X" and unknown

$$\cancel{H^+}\ \frac{[x][x]}{.3} = 1.8E-5$$

$$x^2 = \frac{(1.8E-5)}{.3}$$

$x = 6E-5$
He gets 2.3E-3 Why?

Well, he actually sets up

$$\frac{[x][x]}{.3-[x]} = 1.8E5$$

ICE Table setup? ??

and apparently he is solving the quadratic

Given: 35 ml of HCl of unknown concentration.

· Equivalence point reached w/ 70.05 ml of 0.15M NaOH

It reached equivalent point @ 70.05 ml. Looks very good. Now lets solve it.

$$\text{Mole NaOH} = 70.05\text{ ml}\left(\frac{.15\text{M NaOH}}{1000\text{ ml}}\right) = .0105 \text{ moles}$$

not molar.

So we know from the balanced equation ~~that~~ .0105 mole HCl was also consumed in the reaction and we know that we have 35 ml. What is the concentration?

$$\underset{\text{(molar)}}{\text{Conc}} = \frac{\text{No. moles}}{1000\text{ ml}} = \frac{.0105\text{ moles}}{35\text{ ml}}$$

No. mole = 0.3 Perfect.

Therefore the molar concentration of the HCl is 0.3M which is absolutely correct.

OK, that was good progress with the use of a strong acid & strong base.

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$x^2 = 1.8E{-5}(.3 - x)$

$x^2 = 5.4E{-6} - 1.85E{-5}x$

or ~~$x^2 - 5.$~~

$x^2 + 1.85E{-5}x - 5.4E{-6} = 0$

$x = 2.31E{-3}$ ((Casio solve function used.)
So yes, this is exactly what he did.

$pH = -\log_{10}[2.31E{-3}] = 2.64$

We can definitely check this against ChemLab

Now if the approximate form was used
we would get:

$x = 6E{-5}$
$pH = -\log_{10}[6E{-5}] = 4.2$

We do this by Dec 17 lots ahead

and that is a pretty big difference.

This says to me you better start understanding ICE tables & equilibrium expressions much better.

But out of curiosity, let's check ChemLab.

ChemLab gives us 2.64 exactly!
So now we know what ChemLab is doing and why.

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We do this on Dec 17

So obviously we need to understand ICE tables and equilibrium expressions more clearly.
Back to Moore

257 Schaum . Equilibrium
Schaum does not have ICE tables

Moore (search in index works well), ICE table
Equilibrium p11, p139 - 140, 145

In Moore, there is definitely Ch 14.
Chemical Equilibrium.
and the preceding: Ch 15. Acids & Base.
and now you know why.

So:
at equilibrium, the concentrations of the chemical species are constant, BUT NOT NECESSARILY EQUAL. This was your dissociation problem ~~that~~ you ran into.. Everything is hardly 0.3M on all side of the equation.

What is the origin of the "Reaction Quotient" expression in Chemistry. It is most curious to raise the coefficient to a power.

p 139 Moore

The origin comes from an examination of the "free energy change" within a reaction; this is related to "chemical potentials". Chemical potential is defined as a partial derivative

$$\frac{\partial \Delta \text{Free Energy}}{\partial \text{ amount of the species}}$$

Dec 17 2015 Three Rivers

Therefore it indeed was not so simple.

The origin of the Reaction Quotient calls indeed involves a partial diff equation that relates change in energy to the amount of a substance within a chemical reaction

No wonder that it was not obvious to you where this came from.

Now that we understand where it came from, we can proceed. Back to Moore p 139.

Concentration of solids & pure liquids are assumed to be 1 SINCE THEY DO NOT CHANGE. This actually makes sense

Moore p143

OK lets work with some equilibrium expressions.

This is called the Haber Process, of forming ammonia

$$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_3(g)$$

This says

$$\frac{\underset{.120M}{[NH_3]^2}}{\underset{1.03M}{[N_2]}\underset{1.62M}{[H_2]^3}} = k_c = 3.29E\text{-}3$$

Good.

This is the first time that I have ever actually applied the "Reaction Quotient" principle. It is very cool and powerful.

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So if you know any 2 of the three, ie the product concentration, the reactant concentration, and the equilibrium constant, you can solve for the other.
You must have a balanced reaction to proceed

You can also use your balancer.

$N_2 + H_2 \rightarrow NH_3$

Balances to (with Android App called "Balancing Chemical Equations) to

3.29E-3

$N_2 + 3H_2 \rightarrow 2NH_3$ and actually it is

$N_{2_g} + 3H_{2_g} \rightleftarrows 2NH_{3_g}$

3.29E-3

temperature dependent!!!!!

So now we are given

$N_2 + 3H_2 \rightleftarrows 2NH_3$ = 2.42E-3

2.00M 3.00M

$$\frac{[NH_3]^2}{[2.00][3.00]^3} = 2.42E-3$$

$$[NH_3]^2 = (2.42E-3)(2.00)(3.00)^3$$

NH_3 = 0.36M <u>GOOD</u> you are doing well with this.

The next problem concerns a gas form.

The reaction is:

$$C_{(s)} + CO_{2(g)} \rightleftarrows \underset{1.22\,atm}{2CO_{(g)}}$$

$$\underset{0.780\,atm}{CO_{2(g)}}$$

What we have are two different pressures and no concentration. We also have no K_p. So how the heck do you go about this?

Well guess what? Solids & pure water do not enter into these equations. So:

$$K_p = \frac{1.22^2}{(.780)(1)} = 1.91 \ ? \quad \text{Yes!!!}$$

Very good.

Never include a solid or pure water in an equilibrium expression.

There is a relationship between K_p & K_C

$$K_p = K_C[RT]^{\Delta n_g}$$

We are given $T = 25°C = 298°K$ so we only need Δn_g. What is this?
It is easy actually. It is the difference in moles of gas between the products and the reactants.

$$(2CO) \quad (CO_2)$$

$$\text{So } \Delta n_g = 2 - 1 = 1$$

This means

$$Kc = \frac{Kp}{[RT]^1} = \frac{1.91}{[(.0821)(298)]^1} = .078$$

Good Again!

Next: Given 3.76E-5

$$I_{2(g)} \leftarrow 2I_{(g)}$$

.5M
Given

[illegible]M
~~Calc~~

Actual ans. is 3.76E-5.

No!!!

So $\frac{[\overset{x}{\cancel{1.0}}]^2}{.5} = 3.76E-5$ $x = 4.33E-3\ M$

WRONG WRONG WRONG!!!

This is when the ICE Table was supposed to Come in. You are all wrong. So when do you need an ICE table and when do you not? Why didn't you need an ICE table earlier? What is the difference?

Next page please

Reaction Table (or) (ICE)
ICE Table

Lets begin ice. Page 67

We know the reaction is

$I_2(s) \rightleftharpoons 2I(g)$

3.76E-5

.5M
given

We were also correct in formulating

$$K_c = \frac{[I]^2}{\underset{(0.5M)}{[I_2]}} = 3.76E-5$$

Now, apparently you cannot just solve for I.
Why?

The actual question in the problem is:
"If the initial I_2 concentration is 0.5M, what will be the equilibrium concentrations of $I_2(s)$ and $I(g)$?

Because everything tells you that it is NOT a one way street! He is telling you that I_2 concentration changes also. The double arrow is telling you that also

Moore also says that "looking for a new concentration IS A VERY STRONG HINT to create a reaction table, i.e ICE.

Reaction Table (ICE)
or
ICE Table

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Our first ICE table (A Reaction Table) is another phrase for it, which I tend to prefer since it is descriptive.

	I_2	I	
Initial	0.5	0	
Change	$-x$	$2x$	← This is the critical thought process.
Equilibrium	$0.5-x$	$2x$	

Note: The equilibrium concentration of any substance can never be zero.

2 moles to 1 mole is the ratio so this is why we have 2x. "X" is the change that takes place. The −x comes from the fact that I_2 decreases on the left side and increases on the right side due to the molar ratio.

So now we can reformulate our expression for Kc

$$K_c = \frac{[2x]^2}{[.5-x]} = 3.76E\text{-}5$$

or

You missed this! ↓

$$4\cancel{2}x^2 + 3.76E\text{-}5x - 1.88E\text{-}5 = 0.$$

Quadratic. Casio handles this easily.

x = ~~2.31E-3M~~ ~~3.06~~E-3 M and 2x = ~~6.12~~ 4.32 E-3 M
2.16 I_2 I

but this is change! Not the final concentrations

.5−x = 0.498M I_2 2x = 4.32E-3M I

GOOD HERE ✓

But you made 2 mistakes along the way.

The reaction table is a very enlightening process. It seems like it would be best to use it all the time; I am still uncertain as to how you can avoid using it. Few reactions probably go to completion or are completely one way, & this seems to be what this is about.

It is also fascinating that the molar Concentration of I_2 changed very little. How would you ever have known this w/out going through this process?

You definitely need more practice but you have done @ least the reaction table problem and this is very much to your credit.

I wonder if Chemlab can simulate this?

*
Summary
Dec 17
2015

Summary of Accomplishments

Dec 17 2015 Three Rivers NM

You have been working on some very insightful chemistry problems on the trip and have been learning some very fundamental ideas & processes that underlie chemistry:
These include:

Dissolved Solids

1. Total ~~Conductivity~~ measurements (TDS)
2. Conductivity measurements. (US)
3. Calibrating TDS meter w/ a salt solution
4. Conversion factors (& their range) between TDS & US.
5. Conductivity reference table
6. The impact of filters upon TDS & conductivity
7. The simulation of the above msmts in ChemLab.
8. Introduction to the power of the Pro Version of ChemLab.
9. your prospect of a RMS model for a mixture of ionic species and conductivity
10. Determination of Molecular Weight of a volatile in ChemLab via a Dumas flask & locating alternative simple lab setups on YouTube. This is an incredibly powerful and important technique to have discovered and ChemLab
11. You have modeled dissociation reactions in ChemLab
12. You have modeled strong acid - strong base titrations in ChemLab.
13. We have started to model weak acid strong base titrations and you have a level of success. In the process, however, you have seen the need to understand pH (& how

Summary of Accomplishments

to predict it from concentration knowledge & dissociation constants) and what equilibrium expressions actually mean. More to learn the book.

14. you have a brief review of voltammetry methods
15. You have made some progress w/speedwriting
16. You have equation balancing software now on Android
17. We have worked through a series of Moore problems on titrations, including weak acid - strong base combinations.
18. You have studied pH and you can now predict the ~~con~~ it based upon concentrations, balanced equations & dissociation constants.
19. you understand conjugate acid-base formation & pairs now
20. (Reaction Table (ICE) construction & worked example.

21. you are headed toward developing weak acid - strong base simulations in ChemLab.
You are also headed toward buffer simulation in ChemLab. you would also like to know if you can simulation the ICE reaction in ChemLab also.

Summary of Accomplishments

So you are actually making great progress. You are taking on a multitude of subjects simultaneously so it is no wonder that it seems a bit complex; and yes it is.
But you are doing quite well.

Moore is actually a great book. He is challenging and his problems are not all that simple and they have uncovered numerous mistakes by you.

22. I have now succeeded in modeling & creating st weak acid - strong base titrations in Chemlab!

23. I have started to learn how hydrolysis of a conjugate base relates to the dissociation of a weak acid.
24. A method has been developed, with a great amount of persistence to potentially identify the pKa of an unknown acid!
YES, This appears to have succeeded, Using ChemLab as my Simulator!
Very good work here.

We have now finished Ch14 Moore on Equilibria

Next we would like to walk thru
Ch 15 Acids & Bases
Ch 16 Buffers

We have actually already largely worked through C15 Moore on Acids. We are at the point of duplicating the theory w/in Chemlab.

I see that we are up to Moore p152 where an Reaction Table (ICE) was introduced. Let's take it again from there.

The problem is to determine H^+, and subsequently pH of a 0.3M acetic acid solution.

$C_2H_4O_2$
$CH_3COOH \rightarrow H^+ + C_2H_3O_2^-$

We are given Ka = 1.8E-5

A Reaction Table is a good practice.

	$C_2H_4O_2$	H^+	$C_2H_3O_2^-$
Initial	0.30M	0	0
Change	$-x$	x	x
Equilibrium	$.30-x$	x	x

so we anticipate

$$K_a = 1.8E{-}5 = \frac{[x][x]}{.30 - x}$$

or $x^2 = .30(1.8E{-}5) - 1.8E{-}5x$

or $x^2 + 1.8E{-}5x - 5.4E{-}6 = 0$

$x = 2.31E{-}3$ moles of $C_2H_4O_2$. Therefore the final concentrations are

$$C_2H_4O_2 \leftrightharpoons H^+ + C_2H_3O_2^-$$

$$0.298M \rightleftarrows 2.31E{-}3M \qquad 2.31E{-}3M$$

and now for pH:

$$pH = -\log[H^+] = -\log[2.31E{-}3] = 2.64$$

And now your notes, procedures and simulation of Chemlab on Dec'1st which reproduced the pH exactly are now understood and you are in wonderful position to continue w/ Chemlab on Titrations, esp weak acid strong base titration and then to see if molar concentrations come out correctly and then to create and simulate it yourself in Chemlab and then when all is then working out OK, you will go on to buffers!

The reaction table is a wonderful mechanism because, from it, you can deduce the concentration that result from a given reaction that is a wonderful accomplishment.

It already makes me wonder in a titration how the two different Ka & Kb interrelate w/ one another. Did we not see some kind of relation that $K_a \cdot K_b \overset{?}{=} K_w$? I doubt that.

We started the Chemlab already and then we backed off because we had no idea of the mechanics going on.

Schaum might have a problem of the magnitude.

Yes, Schaum does indeed say that

$K_w = K_a \cdot K_b$

Schaum p285 on tablet covers exactly the question you are asking. It is under the topic of hydrolysis. Hydrolysis means the splitting of water

Schaum p285-286 really is a marvelous section. It even covers it exactly as you need it to.

Indeed we had performed a weak acid titration in ChemLab, acquired some interesting results that we were not able to interpret, and this is where everything stopped.

1. We started w/ 30 ml of $C_2H_4O_2$ (acetic acid) 0.1 M

2. We titrated w/ 0.1 M NaOH. It required 30 ml and the equivalent pH reached was 8.8. And that is when it all got very interesting.

Diss: 3. And in studying VDL file, we have identified that 6! different reactions comprise the total lab. (see earlier notes)

1.76E-5 1. Diss. of acetic acid
Complete? Inst. 2. Diss of HCl This should not apply.
Complete? Inst 3 Diss of NaOH
Inst. 4. Na + Cl Reaction
5.68E-10 5. Hydrolysis of Acetate
1E-14 6. Diss of Water

Now we need to study Schaum & this Lab together to learn what actually happens. Why is it 30 ml? Why is the equivalent pH 8.8?
And yes, I am sure that it is more involved than a strong acid - strong base titration.

Indeed, notice that
(1.76E-5)(5.68E-10) = 10E-15 = 1E-14!
= Kw!

So obviously the topic of hydrolysis is important and also the relationship of

$K_w = K_a \cdot K_b$

What is our general reaction.

$C_2H_4O_2 + NaOH \rightleftarrows C_2H_3O_2^- + H^+ + Na^+ + OH^-$

or

$C_2H_4O_2 + NaOH \rightleftarrows NaC_2H_3O_2 + H_2O$

But as you were saying, this neutralization probably only takes place at a pH of 7.0 when you have water. It is not in any way what happens @ equilibrium w/ various combinations & concentrations.
Within it, we have 2 separate reactions:

$C_2H_4O_2 \rightleftarrows C_2H_3O_2^- + H^+$

$NaOH \rightarrow Na^+ + OH^-$

but Schaum <u>also</u> gives us

Notice! $C_2H_3O_2^- + H_2O \rightleftarrows C_2H_4O_2 + OH^-$

Which is regarded as the splitting of H_2O and this is called Hydrolysis.

Page 78

What Schaum gives us: is

$$C_2H_4O_2 \rightarrow C_2H_3O_2^- + H^+$$

and $$K_a = \frac{[H^+][C_2H_3O_2^-]}{[C_2H_4O_2]}$$

and $$C_2H_3O_2^- + H_2O \rightleftarrows C_2H_4O_2 + OH^-$$

$$K_b = \frac{[C_2H_4O_2][OH^-]}{[C_2H_3O_2^-]}$$

and you can certainly see that

$$K_a \cdot K_b = \frac{[H^+]\cancel{[C_2H_3O_2^-]}}{\cancel{[C_2H_4O_2]}} \cdot \frac{\cancel{[C_2H_4O_2]}[OH^-]}{\cancel{[C_2H_3O_2^-]}}$$

$$= [H^+][OH^-]$$

and this $= K_w = 1E{-}14$.

Notice the Schaum Book has removed all of the problems! This is a serious deficiency.

Let's look @ our reaction in Chemlab and see how it is behaving.

At neutralization the pH is 8.8
We start w/ 30 ml $C_2H_4O_2$ 0.1M

We titrate w/ 30 ml .1 M NaOH

$C_2H_4O_2 + NaOH \leftrightarrows NaC_2H_3O_2 + H_2O$

How about a reaction table?

	$C_4H_2O_2$ +	$NaOH \leftrightarrows$	$NaC_2H_3O_2$	not included? H_2O
Initial	0.1M	0.1M	0	0
Change	0.1-x	0.1-x	x	
Equil.	0.1-x	0.1-x	x	

$$\frac{[x]}{[.1-x][.1-x]} = 1E-14\ (kw)?$$

$$x = 1E-14(.1-x)^2$$

$$x = 1E-14(.1^2 - .2x + x^2)$$
$$x = 1E-16 - 2E-15x + 1E-14x^2$$

$$1E-14x^2 - (1+2E-15)x + 1E-16 = 0$$

x = 1E-16 and we did get a solution without error.

You do not include water in an equilibrium expression so this seems proper to me.
You did get an answer that converged without error so how do you interpret this?

What it says is that VERY LITTLE SALT is formed, ie 1E-16 M concentration.
It also says very little acetic acid & NaOH was used in the process. Does this make any sense.

I would like to see a numerical simulation of this.

I guess a big question is how do you determine the pH of a mixture of an acid & a base? *

Chemwiki tells exactly how to do this and indeed it is quite involved.

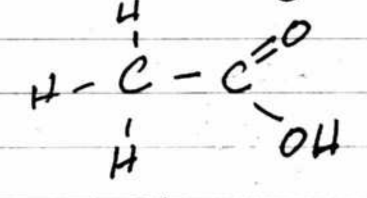
Unfortunately, the PDF created by Web2PDF cannot be opened by Bluefire. But it can be opened by other programs!

We have a pdf saved in My Docs.

Weak Acid - Strong Base
Titration - Begin ChemWiki

ChemWiki Examination.

The first thing we see is that they define acetic acid as $C_2H_5O_2$ instead of $C_2H_4O_2$. I am not sure how they get away with this. Remember CH_3COOH?



There is not room for another H.

Multiple sources show the structure as $C_2H_4O_2$

Indeed it was an error. I wrote to the professor of UC Davis by email; he acknowledged the error and now we know that acetic acid is indeed $C_2H_4O_2$.

1. Find the initial pH.

ChemWiki's Equation (to be fixed) is

$$C_2H_4O_{2(aq)} + OH^- \rightarrow C_2H_3O_2^- + H_2O$$

This is balanced.

So you see the equation focuses on the acid-base portion of the reaction, not the acid-base → salt/water reaction. I am not sure how you would know to do this but it is a pivotal method to understand the real nature of the problem. The Na is transparent to the problem.

Assume 0.3 M $C_2H_4O_2$

[redacted]

ChemWiki Starts Here !

Initial pH of a weak acid

Weak acids apparently require Reaction Tables (ICE)
Reaction tables are actually quite fun; they tell you a great deal about what is happening.

	$C_2H_4O_2$	OH	$C_2H_3O_2^-$	H_2O
init	~~0~~.3M	~~X~~ 0	~~XX0~~ 0	
change	-X	-X	X	
equil	.3-X	-X	X	

$$\frac{[X]}{[.3-X][-X]} = 1.76E\text{-}5$$

Why did they include the water in the expression?

this leads to $\frac{1}{X-.3} = 1.76E\text{-}5 \Rightarrow X-.3 = \frac{1}{1.76E\text{-}5}$
This can't be.

They are counting water in the expression. I did not think this was done.

.3-2.90E-3   2.90E-3M   2.90E-3

What you actually use was

$C_2H_4O_2 \rightarrow C_2H_3O_2^- + H^+$

so

	$C_2H_4O_2$	$C_2H_3O_2^-$	H^+
init	.3M	0	0
Change	-X	X	X
equil	.3-X	X	X

This method makes sense.

or $\frac{X^2}{.3-X} = 1.76E\text{-}5$

Chemlab gives pH as 2.64 GOOD

x = 2.90E-3

$X^2 + 1.76E\text{-}5X - .3(1.76E\text{-}5) = 0$

pH ≠ 2.54

*

Chemworks – Initial pH of a weak acid

Now lets look @ what UC Davis did and Compare it to our own methods & then simulate it within ChemLab.

We can actually simulate the entire problem within ChemLab if we set up HF acid.

$HF \rightleftarrows H^+ + F^-$ $K_a = 6.6E-4$

Reaction Table

	HF	H^+	F^-
Initial	.3M	~~x~~ 0	0
Δ	$-x$	x	x
Equil	$.3-x$	x	x

$$\frac{x^2}{.3-x} = 6.6E-4 \qquad x = .014M$$

so $HF = .286M$
$H^+ = .014M$
$F^- = .014M$

$$\frac{.014\text{ moles}}{1000\text{ ml}} = \frac{x}{25\text{ ml}} \qquad x = 3.5E-4 \text{ moles}$$

$pH = -\log[.014] = 1.85$

Davis gets 1.86 OK

Now lets simulate in Chem Lab

I have done so successfully.
I have 0.3M HF in Chemlab
with a pH of 1.86.

We are doing well.

Dec 19 2015

You are making very good progress. Now you are going to start adding some NaOH to see how it affects the pH.

Back to the titration.

Recall our reaction: .3M HF

$HF \rightleftharpoons H^+ + F^-$ Ka = 6.6E-4

We have done initial pH with HF acid w/ ICE table. Now we add 10 ml. We really do like the idea of the ICE table. > NaOH, also 0.3M.

The reaction he is giving is $C_2H_4O_2 + OH^- \rightarrow C_2H_3O_2^- + H_2O$

Let's try the ICE table

For us, the reaction is then $HF + OH^- \rightarrow F^- + H_2O$

	HF	OH^-	F^-	H_2O
Initial	7.5E-3 mol	3E-3 mol	0	0
Δ				
Equil				

HF $(25ml)\frac{.3M\ HF}{1000ml}$ = 7.5E-3 mol

OH^- $\frac{.3M}{1000ml}(10ml)$ = 3E-3

OK to here, but now we are lost again.

It seems to me that our full equation is actually

$HF + NaOH \rightleftarrows H^+ + F^- + Na^+ + OH^-$

Now if we have 25 ml of 0.3M HF
we have $\frac{.3 \text{ moles}}{1000 \text{ ml}} \cdot 25 \text{ ml} = 7.5E-3$ moles

If we have 10 ml of 0.3M NaOH we have
$\frac{0.3 \text{ moles}}{1000 \text{ ml}}$ 10 ml = 3E-3

Seems like we should be able to construct ICE

	HF	NaOH	H^+	F^-	Na^+	OH^-
Init	7.5E-3 moles	3E-3 moles	0	0	0	0
Δ	~~7.5E-5~~-x	-3~~0~~E-3	X	X	Y	Y
Equil	7.5E-3-x	~~3E-3~~ 0	x	x	y	y

$$\frac{x^2}{7.5E-3-x} \overset{?}{=} 6.6E-4$$

$$x^2 + 6.6E-4x - (7.5E-3)(6.6E-4) \overset{?}{=} 0$$

$x = 1.919E-3$

so $pH \overset{?}{=} -\log(1.919E-3) =$

$pH = 2.72$

Chemwiki gets 3.0

So I am close, but not exact

Skip for Titration

Dec 18 2015 Elev ~ 4500'
Three Rivers NM - On Car Dash, Windows Open @ Stove

SNX	Time	PM2.5	T°C	WIND	% RH	Est Vis
Clear	1400	19	27.1	2-4 ~~03~~	4% ~~35%~~	80+ mi
No Traffic	1405	18				
Sunny	1410	24				
	1415	25				
		$\bar{X} = 21.5$				

WY							
Clear	On Car Hood:	PM2.5	T°C	WIND	% RH	ELEV	VIS
Sunny	1430	2	19°C	2-4mph	4%	~4500	80+ mi
No Traffic	1435	4					
Mem 1	1440	1					
	1445	2					
		$\bar{X} = 2.25$					

Notes: Ideal weather conditions. Some light haze visible over ~~40~~ 30+ miles distance. Memory # 1

Mem #1 1502 2 18°C 2-4mph 5% ~4500' 80+ mi

12-19-2015 Three Rivers Camp NM
Mem 2 1230 2 17°C 1-4 mph 13% ~~10%~~ 5500 70+ mi
Mostly Cloudy, stratocumulus, little to no traffic

Mem 3 12-20-2015 Three Rivers Camp NM
1030 2 18°C 10mph 18% 5500 80 mi
Mostly Clr, Cumulus, no traffic

12-20-2015 Three Rivers Camp
1400 14 18°C 22mph 30% 5500 60 mi
Mem 4 Clr, Windy, No Traffic

you actually seem to be on the right track to me. You get a pH of 2.72 and Chemwiki gets 3.0 so I am actually pretty close & it is hard to say why I would be wrong.

Apparently, however, it is time to start learning about the Henderson-Hasselbalch Equation. Let's find it.

Ka of acetic acid is 1.8E-5

Acetic Acid has a pKa of 4.76

What is a pKa?

pKa is nothing more than the -log of Ka!

$pKa = -\log(Ka)$

Also we learn that the Henderson equation is nothing more than an alternate form of the equilibrium expression that is useful when you know the ratios of base and acid.

So, for example

$pKa = -\log(Ka)$

since we know Ka for acetic acid is 1.8E-5

$pKa = -\log(1.8E-5) = 4.74$

which guess what, is exactly what Kevin Ahern has on p 17 in Biochemistry Free & Easy.

The HH equation is of the form

$$pH = \underset{\overset{\uparrow}{\text{this is just a number}}}{pKa} - \log\left(\frac{[HA]}{[A^-]}\right) \swarrow \text{this is just a ratio.}$$

So obviously this is valuable when you know the ratio of acid to base, or vice versa. And that is what HH is all about.

Now we have this under our belt. It means that we might have been able to solve our problem this way.

So if we knew the ratio of acid to base then would also take care of the problem. Do we know? Well, we see now that our ice table is wrong.

	HF	NaOH	H^+	F^-	Na^+	OH^-
Init	7.5E-3 moles	3E-3 moles	0	0	0	0
Δ	-3E-3 moles	-3E3 moles	X	X		
Eq.	4.5E-3	0	X	X		

or $\frac{X^2}{4.5E-3} \overset{?}{=} 6.6E-4$ $X = 1.72E-3$

Now you get $2.76 \approx 2.8$ vs 3.0

Again, it seems close, and I do not know why this would be wrong. It may not be. Let's keep going.

Chemwiki
#2

adding a "little bit"
of NaOH to a weak acid
(ie, less than equilibrium

Now we are going to have added 12.5 ml NaOH

	HF	NaOH	H^+	F^-	Na^+ ~~OH~~	OH^-
Init	7.5E-3 moles	0 3.75E-3 moles	0	0	0	0
Δ	-3.75E-3	+3.75E-3	x	x	y	y
Eq	3.75E-3	3.75 ~~0~~ E-3	x	x	y	y

HF: 25ml = 7.5E-3 moles
NaOH: 12.5ml = $\frac{0.3 \text{ moles}}{1000 \text{ ml}}$ 12.5 ml = 3.75E-3

$$Ka = \frac{[H^+][F^-]}{[HF][NaOH]} \Rightarrow \frac{x^2}{3.75E\text{-}3^2} = 6.6E\text{-}4$$

?

x = 1.573E-3 9.63E-5

pH = -log (1.573 E-3) = 2.80 Wrong 4.02 too [illegible]

We are always running a little lower.
He has pH = 3.18

There does seem to be a problem here
of some kind.

12.5 ml addition _ HF - NaOH   CW#2
Chemwiki

It looks like we need to look @ the ratio of acid to base.

$$pH = pKa - \log\left(\frac{HA}{A}\right)$$

$$\log(1) = 0$$

$pH = pKa$ $pKa = -\log(Ka)$
$= -\log(6.6E-4)$
$= \underline{\underline{3.18}}$ $\underline{\underline{\text{got it}}}$

Ok, the problem was

1. Your ICE table was formed improperly but you were close
2. You did not take advantage of the HH equation which ultimately only require a knowledge of ratio of acid to base.

Now repeat 10 ml added; Now we can go back & learn the proper ratios.

only thing needed

	HF	$NaOH$	$\rightleftharpoons$	H^+	F^-	Na^+	OH^-
Init	7.5E-3 moles	3E-3 moles		0	0	0	0
Δ	-3E-3	-3E-3		3E-3	3E-3		
Eq	4.5E-3	0					

$$\frac{HF}{F^-} = \frac{4.5}{3}$$

$HF\ 25ml \ni \frac{0.3 \text{moles}}{1000 ml} 25 ml = 7.5E-3 \text{moles}$

$NaOH \ni \frac{0.3 \text{moles}}{1000 ml}(10 ml) = 3E-3 \text{moles}$

$$\frac{4.5E-3 \text{moles}}{35 ml} = \frac{X}{1000 ml}$$

$X = .1286 M$

Chemwiki 10 ml addition

Lets try this:

$pH = pka - \log\left(\frac{HA}{A}\right)$ $pH = pka + \log\left(\frac{A^-}{HA}\right)$

$= 3.18 - \log\left(\frac{4.5}{3}\right) = 3.00$

Yes, this is perfectly correct.

So proper construction of the ICE table is critical to success & this can take some thinking.

The next example is adding 25 ml NaOH

~~H~~

	HF	NaOH	⇌	H^+	F^-	Na^+	OH^-
Init	7.5E-3 moles	7.5E-3 moles		0	0	0	0
Δ	-7.5E-3 moles	-7.5E-3 moles		7.5E-3	7.5E-3	7.5E-3	7.5E-3
Eq	0			1			

Ratio of acid to ~~base~~ = 1 NO IT IS NOT, IT IS ZERO!

$pH = pka - \log\left(\frac{HA}{A}\right)$

$= 3.18 - \cancel{\log(-1)} =$ $\log(-1)$ is not a real number.

You have it very wrong

One lesson is that the HH equation fails @ equilibrium. Equilibrium calls for some advanced thinking. F hydrolyzes.

You have it very wrong. Let's see why. You have the ICE table pretty much correct. You did forget to finish it.

The acid base ratio is $\frac{0}{1}$ and the log of 0 is undefined.

What if we chose a very small value for HF instead.

$pH = pKa - \log\left(\frac{HA}{A}\right) \approx 3.18 - \log(.001)$ eg.

This gives us 6.18 The actual answer is 8.18 so now you see why the pH is

Now try .00001
and we get, wa la 8.18 !!!

so ~~this can work. Very interesting~~.

This was just luck. If you had picked .0000001 you would get pH = 10.18 So this idea can not be used. What it does tell you is that pH is changing very quickly when the acid/base ratio approaches zero.

So apparently we must realize ~~that hydrolysis~~ hydrolyze of F^- is taking place. I had no idea to look for that. What is it?

Notice the pH is not, however, 7.0 @ the equivalence point. This too, is interesting.

Time to learn about Hydrolyze.
Schaum has one section on this.
Let's also look @ Zumdahl.

Zumdahl has a very extensive discussion on this problem. p 733 - 739.

Let's get the definition of hydrolyze and hydrolysis:

From Oxford, hydrolysis & hydrolyze are both involved in the decomposition of a substance that combines w/ water.
Let's see if this holds to the case.
Look @ Schaum first.

From Schaum, hydrolysis means literally splitting water. An example reaction is

$$C_2H_3O_2^- + H_2O \rightleftarrows C_2H_4O_2 + OH^-$$

acetate ion

a basic solution is produced.

$$K_b = \frac{[C_2H_4O_2][OH^-]}{C_2H_3O_2^-}$$

Schaum says that
hydrolysis involves a reverse of acid dissociation.

Schaum also says that hydrolysis applies to any species which is the conjugate base to an acid having an ionization constant Ka.

Then, it seems to me, any time that you have a weak acid, you also have hydrolysis of the conjugate base.

Example: Acetate ion $C_2H_3O_2^-$ is the conjugate base to acetic acid. Acetic acid has a Ka. Thus the acetate ion is subject to hydrolysis.

So hydrolyze seems to mean
1. Combining w/ water
2. splitting the water up into H^+ and OH^-
3. combining w/ either the H^+ or the OH^- to make something new.

Many metal ions hydrolyze. Look @ iron Fe^{+3} for example!

$$Fe^{+3} + H_2O \rightleftarrows Fe(OH)^{2+} + H^+ \qquad Ka = \frac{[H^+][Fe(OH)^{2+}]}{Fe^{3+}}$$

Tell me this isn't interesting.

So now that we supposedly know what hydrolysis is (Combining w/ a splitting of water along w/ a recombination)

let's see if we can now apply it to the HF titration example.

Recall that we had a reaction:

$HF + NaOH \rightleftarrows H^+ + F^- + Na^+ + OH^-$

and that we neutralized it eventually w/ 25 ml NaOH.
Now we are trying to find the pH @ this point but we ran into a problem w/ using the HH equation because log(0) is undefined.
Apparently hydrolysis is involved.
Let's see how and why?

He says "F^-" will hydrolyze.

OK, this makes sense now

$F^- + H_2O \rightleftarrows HF + OH^-$

$\frac{7.5E-3 \text{ moles}}{50ml} = \frac{X}{1000ml}$ $X = 0.15M$ solution

We know now that the HF is contained within 50ml of total solution. So it seems to me that we have a a concentration.   why?

We have a problem here, it is $\underline{0.15M}$

$\frac{0.3 \text{ moles}}{1000ml}(50ml) = .015M$ solution of HF and this agrees w/ his ICE.

Seems to me that our table is

	F^-	$H_2O \Leftrightarrow$	HF	OH^-
Init	0	50ml	.015M	0
Δ	X		−X	X
Eq.	X		.015−X	X

$K_b = \frac{(.015-x)}{x}(x) =$

$.015 - x = 1.5E-11$

$x = .015 - 1.5E-11$

and we know that $K_w = \cancel{K_a \cdot K_b}\ K_a \cdot K_b$

a $K_b = \frac{K_w}{K_a} = \frac{1E-14}{6.6E-4} = 1.51E-11$

So now we can set up

$\frac{(.015-x)}{x}(x) = 1.51E-11$

or $.015x - x^2 = 1.51E-11x$

or $x^2 + 1.51E-11x -$.

We made a big mistake
on the original HF concentration.
NO GO.
Repeat.

You made a major mistake that affects everything you show in the ICE table.

You determined the initial concentration of the HF incorrectly.

What you know is that your original concentration of HF is 25 ml of 0.3M HF.

or $\frac{.3 \text{ moles HF}}{1000 \text{ ml}} * 25 \text{ ml} = 7.5E-3$ moles

in 25 ml
But now you know this same no of moles is contained in 50 ml of neutralized NaOH - HF so it is

$$\frac{7.5E-3 \text{ moles}}{50 \text{ ml}} = \frac{x}{1000 \text{ ml}} \quad x = 0.15M$$ solution

or an even simpler way is that 0.3 M was diluted in half to from 0.3 to 0.15M!
Either way is fine.

Now, you propose the hydrolysis reaction as

$F^- + H_2O \rightleftharpoons HF + OH^-$ it is balanced

$-.15 - Y = 1.5E-11$

Page 98 $+ .15$

$Y = .15 - 1.5E-11 \quad X =$

Something is apparently very wrong w/ my reaction table.

You therefore propose a reaction table as

	F^-	H_2O ⇌	HF	OH^-
init	0	—	0.15M	0
Δ	$-X$		$.\,+X$	X
eq	$-X$		$.15+X$	X

Now it is true that $K_w = K_a \cdot K_b$
so since we have OH^- we need to solve for K_b

$$K_b = \frac{K_w}{K_a} = \frac{1E-14}{6.6E-4} = 1.51E-11$$

So our proposal is

$$-\frac{(.15+X)(X)}{\cancel{-X}} = 1.51E-11$$

but this is not his proposal!

His proposal is:

$$\frac{[H^+][F^-]}{[HF]} = \frac{X \cdot X}{0.15-X} = 1.515E-11$$

or $\frac{X^2}{0.15-X} = 1.515E-11$ or $X^2 + 1.511E-11X - (.15)(1.515E-11) = 0$

$X = 1.507E-6$

$-\log(1.507E-6) = 5.82$
and then he goes $14 - 5.82 = 8.18$ His Answer

and we, of course, have some serious questions on the matter.

I therefore need an example of
a weak acid hydrolysis reaction table
(ICE)

Ok, now we have a better definition of hydrolysis:

Hydrolysis is the breaking of a bond in a molecule using water.

That already changes everything.

This means we are dealing w/ the reaction

$$H_2O + HF \rightleftharpoons H^+ + F^- + OH^-$$

and what you are doing is breaking the bond of water just like you understood.

This changes everything. A new reaction table is in order now.

I wonder if the reaction is the other direction! But we know that it actually can go either way.

We know now that the molar concentration of HF is 0.15M @ the equilibrium point.

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Equilibrium Point
of Titration - ChemWiki

Let's work a a reactn table.

	H_2O	HF	$\rightleftharpoons H^+$	$+ F^-$	$+ OH^-$
init	—	.15	⊗	0	0
Δ		~~.15~~ -x	x	x	?
eq		.15-x	x	x	?

And now we match this as

$$\frac{x^2}{.15-x} = K_b$$

We know that $K_b = 1.51E-11$

What is really interesting to me that we use an acid dissociation (but apparently it is actually a hydrolysis reaction) to solve for K_b. What happened to the OH^- in the picture?

and now we solve for K_b @

$$x^2 + 1.51E\text{-}11x - (.15)(1.51E\text{-}11) = 0$$

$$x = 1.507E\text{-}6$$

$$pOH = -\log(1.507E\text{-}6) = 5.82$$

and $pH = 14 - 5.82 = \underline{\underline{8.18}}$ which is correct.

So my main question is how did we know that we were solving for K_b when the entire reaction he set up as a secondary phase seems to involve the dissociation of HF and ignores the creation of the OH^- ion entirely. This is not clear to me.

This is, however, a most fascinating process to work through.

Lesson also: HH fails @ the equilibrium point.

[redacted]

Now we move on past the equilibrium point:

But before, first pause on molar concentration of $FeSO_4$ heptahydrate [redacted]

$FeSO_4 \cdot 7H_2O$ 278.01

278.01 MW

$$\frac{0.15\text{gms}}{.30\text{ml}} = \frac{\overset{5\text{gms}}{X}}{1000\text{ml}} \quad X =$$

$$\frac{5}{278.01} = \underline{.018M}$$

Ok lets continue w/ titration:
Now we add 26 ml of NaOH
so we have passed the equilibrium point.
Now do we want to try to think this out
or go to the answer right away?
Our original equation is

$$HF + NaOH \rightleftarrows H^+ + F^- + Na^+ + OH^-$$

But we also learned of hydrolysis @ the point of equilibrium

$$HF + H_2O \rightleftarrows H^+ + F^- + OH^-$$

We also learned of the value of the HH equation where only the acid base ratio is required.

[redacted]

Problems. Need to consult w/Chemwiki

[redacted]

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Now, would we like to hazard a guess. I would still like to use the HH equation since it is so simple. Let's try it before we go to Chemwiki.

	HF	NaOH	⇔ H^+ +	F^- +	Na +	OH^-
Init	7.5E-3moles	7.8E-3 moles	0	0	0	0
Δ	-~~7.5E-3~~-x	-7.5E-3	~~7.5E-3~~ x	~~7.5E-3~~ x		
? eq.	7.5E3 0 -x	0.3E-3	x	x		

HF is always 25 ml so it remains as

this is

$\frac{0.3 moles}{1000 ml}$ (25ml) = 7.5E-3 moles

Now we have 26 ml of NaOH

$\frac{0.3 moles}{1000 ml}$ (26ml) = 7.8E-3moles

6

Well, I think HH works only up to the point of equilibrium.

$\frac{X^2}{.3E-3} = 6.6E-4$?

X= 4.45E-4

pH = 3.35

pOH 10.65

None of this makes any sense.

Now we must go to Chemwiki. HH does not ap

Ok, it is not hard.
Here we go.

Once equilibrium has been passed, here is the reasoning. It is fairly simple actually.

We know we have
25ml 0.3 mol HF = 7.5E-3 moles HF

28ml 0.3 mol NaOH = 7.8E-3 moles NaOH

only 7.5E-3 mole NaOH was needed to neutralize, therefore we have left over

$$\begin{array}{r} 7.8E-3 \\ -\ 7.5E-3 \\ \hline =0.3E-3 \end{array} \text{ moles NaOH}$$

Since we know that

$$\begin{array}{ccccc} NaOH & \rightarrow & Na^+ & + & OH^- \\ 0.3E-3 & & 0.3E-3 & & 0.3E-3 \\ & & \text{moles} & & \end{array}$$

So we have 0.3E-3 OH^- left over in a total volume of

$$\begin{array}{r} 25\text{ ml} \\ +\ 26\text{ ml} \\ \hline 51\text{ ml} \end{array} \quad \text{so} \quad \frac{0.3E-3\text{ moles}}{51\text{ ml}} = \frac{x}{1000}$$

x = 5.88E-3 Molar Solution of ~~NaOH~~ OH^-.
What is its pH?

Week Acid - Strong Base Titration - End ChemWiki

and if you understood what pH + pOH are really about, you have everything you need.

By definition

$pH = -\log(H^+)$

$pOH = -\log(OH^-)$

so $pOH = -\log(5.88E-3)$

$= 2.23$

so $pH = 14 - 2.23 = \underline{\underline{11.77}}$

and this IS it!

It is all you had to do.

So you have learned quite abit:

SUMMARY

1. HH can be used up to equilibrium point
2. Equilibrium point cannot use HH and hydrolysis is involved. It is indeed trickier
3. HH can not be used past the equilibrium point.
4. Past equilibrium is actually quite simple, just determine concentration of left over OH^- or H^+ as the case may be.

This whole process was fascinating
Totally dependent upon ChemWiki articles.

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We have done some very good work and I now have a much better sense of what acid - base chemistry is about.

Two more followthroughs :

1. Example 6 on ChemWiki article should be done

2. Predict $Fe(OH)_2$ pH levels - can you?

[redacted]

Let's do the equivalence example w/ ChemWiki - the last problem.

Given

means molar

$CH_4O_2\ H_4$

15 ml of M CH_3COOH 0.15M

0.1 M NaOH ← acetic acid

Question: How many moles NaOH to reach the equivalence points

~~CH_3COOH~~

$$C_2H_4O_2 + NaOH \rightleftharpoons C_2H_3O_2^{-} + Na + \overset{+\,OH^-}{H^+}$$

We can always set up a reaction table which we fear.

$C_2H_4O_2 + NaOH \rightleftharpoons C_2H_3O_2^- + Na^+ + OH^- + H^+$

is this balanced? yes.

Init
Δ
Eq

$C_2H_4O_2 \quad \frac{0.15 \text{ moles}}{1000 \text{ ml}} (15 \text{ ml}) = 2.25E{-3} \text{ moles}$

$NaOH: \quad \frac{0.1 \text{ moles}}{1000 \text{ ml}} (X \text{ ml}) = 2.25E{-3} \text{ mole}$

required to neutralize

$X = \underline{\underline{22.5 \text{ ml}}}$

and yes, indeed, this is the correct number!

It is true that $C_aV_a = C_bV_b$

or $V_b = \frac{C_aV_a}{C_b} = (\cancel{15 \text{ ml}}) \frac{(.15)(15 \text{ ml})}{.1}$

$= 22.5$

This is the short cut method, which does indeed work.

Dec 19 2015

What if we now try to simulate all of the work that we just did w/ HF & NaOH on ChemLab?

0.3 M HF ChemLab's pH checks in perfectly @ [illegible] 1.85

Titrate w/ 12.5 ml NaOH checks in w/ pH perfectly @ 3.10

Now ~~we~~ go to 25 ml

Something very wrong happened here.

After 12.5 ml it blew up. pH jumped up prematurely to 13 ml

Something very wrong here.

Ok, ours w/ HF & NaOH is wrong.

However acetic acid & NaOH demo looks to be behaving perfectly.

A perfect match @ 30 ml w/ 0.1 M NaOH vs 0.1 M $C_2H_4O_4$.

Therefore, you are the one with problem.

Fix it!

We could certainly do our compare now w/ acetic acid & NaOH & we know that they will match Chemcad.
This is a great example of complete knowledge of the process is required to simulate it properly.

[redacted]

PM 2.5 Monitoring Pop Dens

Page 109 Dec 23 Omega Case No. 1842778 Problem Logged w/Omega

12-21 Alamogordo Town 2

Partly Sunny, Stratus

Mem6 1500 23.1°C 13 PM2.5 6.2% RH Wind 3 from NW

Photo 60 mi Vis Elev ~ 4500', No traffic

Three Rivers Camp, Partly Sunny, Stratus 0

No Photo 1630 10°C 2 PM2.5 30% Wind 2 from W

80 mi Elev 5500, No traffic

12-22-31 Three Rivers Camp, Partly Sunny, Stratus 0

Mem 7 0900 16°C 2 PM2.5 17% Wind 5 from W

80 m Elev 5500 No traffic

Pop Density Scale will be population at site

0 ~~≤ 100 sq~~ m. < 100 people

1 ~~≤ 100~~ < 1000

2 < 10,000

3 < 100,000

4 500,000 +

Kirsten Peters

Mem 8 12-23-31 TR Camp, Stratus, Cloudy

0815 6°C 2 PM2.5 67% RH Wind 8 from W. Pop 0

80 m Elev 5500 None visible (Stratus)

12-24-31 TR Camp, Cldy, Stratus

Mem 9 0800 7°C 2 PM2.5 67% Wind 4 from W Pop 0

70 m Elev 5500 None visible (Cldy)

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12-25-31 TR Camp Partly Cloudy, Cumulus
Mem10 0745 11.5°C 2 PM2.5 42% RH Wind 15 from W Pop 0
80mi Elev 5500 No Traffic

No 1130 TR Store Mostly Sunny, Cumulus
Memory 1130 22°C 25 PM2.5 16% RH Wind 15 from S. Pop 0
50 mi Elev 4500 No Traffic

Mem 11 1345 Denny's (Indoors) Restaurant, Alamogordo NM
25°C 21% RH 45 PM2.5
Restaurant @ full capacity, Carpeted Floor

1530 Alamogordo Town Cirrostratus, Partly Sunny
1530 24°C 10 PM2.5 11% RH Wind 10 from S. Pop 2
60mi Elev 4500' No Traffic

1600 Tularosa Town Partly Sunny, Cirrostratus
1600 23°C 5 PM2.5 12% RH Wind 15 from S Pop 1
60 mi 4500' No traffic

1630 2 miles W of Three Rivers Store
1630 23°C 20 PM2.5 23% Wind 20 from S Pop 0
30mi 4500' No traffic
N. of White Sands, Dust Storm in Progress

Dec 26 2015 TR Camp NM
~~Pop 0~~
0830 Pop 0 WX Stratus, Light Snow VisTraffic None PM25 2
T° 8°C Wind 1 from N %RH 45 Elev 5500 Vis 40mi Mem 12

Dec 22 2015
Continuing w/ analysis of Chemlab

We start by studying the existing weak acid strong base titration w/in Chemlab.

Reaction given as

Diss. of acetic acid
  Reactants - Acetic Acid
  Products - Acetate ion, Hydrogen Ion

Acetic acid is 0.1 M Stock, Solution
  Solubility is listed as 1060., Heat Capacity is 50.
Acetate Ion is a reaction product only
Hydrogen Ion is a " " "

The acetate ion is largely empty other than
  MW
  CAS No. (it looks generated)
& Charge (in -1)

Hydrogen ion in the same way with 1.0 as Charge.

Now let's look @ our VDL.
  1. Reaction..
    Acetic acid chemical definition is the same
    Stock, 0.1 is ok also.

    Acetate Ion is a reaction product ok
    Acetate ion ok in the database also.

Hydrogen ion looks OK as reactant product also.
Hydrogen ion looks OK as ion also.
Everything is yellow except MW, CAS No, ion state and charge. It is also designated as a solid fill so that you can see it.

So I see nothing wrong w/ the acetic acid designation.
w/in my VDL

Now let's go to NaOH within ChemLab demo lab.
NaOH: reactants, sodium hydroxide
products, sodium cation, hydroxide ion
NaOH is defined OK.

Interesting: Sodium cation does not have a 1.0 charge on it. This looks like a mistake!
This is wrong.
I wonder how the titration works without it.
Let's check my VDL.
My VDL is missing it also.

So how did the ChemLab default titration ever work? Probably because Na+ is not @ all involved in the reaction of acid base chemistry. It will be involved in the formation of the salt. Let's move on

$C_2H_4O_2 + NaOH \rightarrow C_2H_3O_2^- + H^+ + Na^+ + OH^-$

The primary components all seem to be in order.

But something else is in need here.
Our problem is occurring @ the equivalence point. We know that this likely involves

As you recall the hydrolysis issue was a bit confusing because you were actually measuring the OH^- even though the hydrolysis reaction seems to involve the acid.

Recall what we had that seemed to be the best fit $H_2O + HF \Leftrightarrow H^+ + F^- + OH^-$
We chose the following to work with in combination w/ ChemWiki
For us, this would now equate to:

$$C_2H_4O_2 + H_2O \Leftrightarrow C_2H_3O_2^- + H^+ + OH^-$$

Now, the big question is, do we have a reaction of this sort listed in ChemLab?

Guess what: We do indeed have one called Hydrolysis of acetate. This is likely very important. The details of the reaction are:
Reactants ~~Products~~: ~~Acetic Acid~~ Acetate Ion, water
Products: Acetic Acid, Hydroxide Ion.

This is fascinating, it is not what you had before and yet this is in keeping w/ your study of what hydrolysis is as a reverse reaction.

Let's make sure the reaction is in my VDL
And we will settle theoretical differences later.

Somehow we do seem to have all the reactions
duplicated, probably from copying the file.
So I have to wonder, why is it messed up?

Is it only HF that is messed up?

Yes, the ~~$H_2C_2O_2$~~ $C_2H_4O_2$ titration in mine is fine!
The problem was indeed w/ the HF.

HF hydrolysis is probably ill defined.

Ok, let's go back to this hydrolysis issue.
We undoubtedly need to have the hydrolysis of
(ChemLab default) It is called "Hydrolysis of acetate")

This means we must have a "Hydrolysis of Fluoride"!
It will need to be

$$F^- + H_2O \rightarrow HF + OH^-$$

Reactants will be Fluoride Ion & water.
Products will be HF & OH^-

I am sure that we do not have this.

Guess what: There is an equilibrium constant
defined for the hydrolysis of the acetate ion.
It is 5.682E-10. Let's check it.

I did check it, and yes it all stems from the relation:

$K_w = K_a \cdot K_b$

For acetic acid, we know that $K_a = 1.8E-5$
We know that $K_w = 1.0E-14$
We can solve for K_b as $5.56E-10$

and then is apparently the K_b which is apparently what corresponds to hydrolysis. The actual value given in ChemLab is $5.68E-10$, so that is indeed very close.

This is a pivotal understanding *

So in a way, we can think of hydrolysis of a conjugate base as being the inverse of the dissociation of a weak acid.

So in our case for HF
$K_a = 6.6E-4$

This means $K_b = \dfrac{1E-14}{6.6E-4} = 1.51E-11$

and we demonstrated how often this number showed up before! So now we know the hydrolysis equilibrium constant for HF, which is also the same as K_b.

Now that we have defined the reaction,
let's try the titration of ~~acetic acid~~
Hydrofluoric acid w/ NaOH

~~And this did not work either~~.
This is fantastic! I have succeeded.

I have therefore succeeded in creating, from scratch, my own weak acid- strong base titration! This opens up many possibilities now.

1. Conductivity
2. MW Determination of a volatile fluid
3. Strong acid - strong base titration
4. Weak Acid - Strong base titration.

This is great! This is very cool what has happened here. Success has been achieved w/ the file=

Weak Acid Titration Dec 22 2015 -02. lab
& the accompanying ~~URL~~ file UDC format.

Everything looks very good.

Lets Check it.

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Form Chemwiki PDF ChemLab Paper Chem Wiki

Start w/ 25 ml 0.3M HF
Starting pH is 1.86 OK ✓

Add 10 ml NaOH pH = 3.02 vs 3.00 good ✓

Now add 2.5 ml additional
Total = 12.5 ml pH = 3.19 vs 3.18 ✓

Now add 12.5 ml add (for a
Total = 25 ml) pH = 8.50 vs 8.18 ✓

Now add 1 ml (for a
Total = 26 ml) pH = 11.77 vs 11.77 ✓

I now have a marvelous simulator of arbitrary weak acid & a strong base titration.

Questions before me;

1. What happens with a weak acid and a weak base?

2. How do you make a buffer? How do you know when you have one? How do you know how good it is?

Lets try a weak acid or a weak base for kicks.

There is a big question as to whether or not you should seek an understanding of the dynamics of a weak acid, weak base titration. It does not actually sound very practical or useful since the equilibrium point is difficult to define.

Question: Does Zumdahl cover this? This could be a criteria to use.

2nd. Now that we understand titration better, How do we apply it? How about the unknown acid titration in Chemlab?

3. It is buffer time. Buffers are a very big deal and we need to learn about them.

Zumdahl does not cover weak acid - weak base titrations so it seems like we can bypass that for now.

Lets review the strong acid - strong base titration before we proceed.

You do not need Ka for acids that dissociate completely. You only need to know the no. of moles of H^+ in the dissociation equation. (Not molar concentration - you will see that there is a difference) - you just need the actual no of moles.

$$HA \rightarrow H^+ + A^-$$

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Titration Applications

Dec 23 2015

It seems, therefore, that we can proceed toward buffers soon. However before doing so we need to understand the applications of titration.

1. We can determine ~~pK~~ Ka if we know the concentrations.

2. We can titrate and see what kind of curve we get. This tells us if it is a strong acid or a strong base.

3. Maybe we can determine equilibrium constants?

4. We should be able to determine concentration.

—

From E-how.com there are many many uses of titration.

1. A process or method to determine the concentration of a substance in a solution; a known reagent is added to a solution of unknown concentration. (electrical or chemical methods)

Titration Applications

Uses of Titration

2. Pharmacists
3. Monitor blood glucose levels
4. To define oils, fats & other substances
5. Free fatty acid content
6. Unsaturated fatty acids
7. trace amounts of water
8. Estimated chain length of fatty acids in a fat
9. Tests for amount of salt, sugar, Vit C or Vit E
10. Anesthesia concentration
11. High school chemistry
12. Biodeisel production; determine acidity of waste veg. oil
13. Maintain aquarium water
    Balance pH, ammonia, nitrate & nitrites
14. Determine concentrations of chemicals of interest in blood & urine

15. There are various types of titration:
    1. acid-base
    2. reduction - oxidation
    3. precipitation
    4. Complexometric

So there are many many applications to research. Let us at least do the unknown acid in Chemlab to get one application.

It also seems that you could simulate the equilibrium constant.

16. To define a protein?
17. Determine the pKa of an unknown acid? Yes!
    My method has been developed.

Chemlab

We are titrating an unknown acid. Using "A". We have 35 ml and actually we know that it is HCl, but we will pretend that we do not, and also it is of unknown concentration.

We do, however know the pH. It is 0.96 I wonder if there is a way we know if an acid is a strong acid or not. We do know that pH is certainly a clue.

We can therefore make a strong presumption that it is a strong acid. So

$HA = H^+ + A^-$

I do think we need to titrate it. The pH is not enough to know how concentrated it is?

$pH = -\log[H^+]$ or $\log[H^+] = -pH$

or $H^+ = 10^{-pH}$ or $H^+ = 10^{-.96} = 0.11$ ✓

So since there is complete dissociation we conclude that it is 0.11 M HCl.

But now lets titrate.
With 0.1 M NaOH.

We have a very clean titration w/ equilibrium @ pH 7.0
The verification that it is a strong acid that
Completely dissociates.

The equivalence point occurred @ 38.5 ml
We know when we have Complete dissociation that we
Can use

$$C_a V_a = C_b V_b \quad \text{or} \quad C_a = \frac{C_b \cdot V_b}{V_a} = \frac{0.1M(38.5ml)}{35ml}$$

$= .109M\ HCl = 0.11$ ✓

Which is exactly what we got. Very good. So titration was not technically required since we have an accurate measurement of pH.

Lets go to the second acid: "B"
$pH = 1.05$

But we know that $H^+ = 10^{-pH} = 10^{-1.05}$
$= 0.089M\ HCl = 0.09M$ ✓

Titration result: 27 ml
so we know that $C_a = \frac{C_b \cdot V_b}{V_a} = \frac{0.1M(NaOH) \cdot 27ml}{30} = \underline{\underline{.09M}}$ ✓

a match:
And Acid #3 (C): pH meas = 1.10

so $H^+ = 10^{-1.10} = 0.079M = 0.08M$ ✓

Titrate with 24 ml so $C_a = \frac{(0.1M\ NaOH)(24ml)}{30ml} = 0.08M$ ✓

[redacted]

These titrations were perfect, about the simplest case possible w/ strong acid - strong base combination.

There are many good opportunities before us with titration. It is low tech & inexpensive to do. This can be explored in great depth w/ the examples given before.

I think that we can go to buffers now.

I am very surprised that Zumdahl puts buffer before titration. Moore certainly did not.

We are going to <u>start</u> w/ Moore:

A buffer contains a weak acid and its conjugate base. HA & A^-

Just like we have been studying!

The HH equation is used to calculate the pH of a buffer.

$$pH = pKa + \log\left(\frac{A^-}{HA}\right)$$

The more concentrated the acid & base are, the greater the buffer capacity.

Here is an example:

Given 2 moles of Ammonia (NH_3)
3 mole of Ammonium Chloride NH_4Cl
1 liter of solution
$K_b = 1.81E-5$

Question: What is the pH?

What is the reaction?
Question: Isn't ammonia an amine?) Remember Amine a NH_2R
NHR_2
NR_3

~~$NH_3 \Leftrightarrow NH_4$~~

$$\underset{(aq)}{NH_3} + \underset{(l)}{H_2O} \Leftrightarrow \underset{(aq)}{NH_4^+} + \underset{(aq)}{OH^-}$$

So notice how this is different from an acid
Acid $HA \Leftrightarrow H^+ + A^-$ (proton donor)
Base $HB + H_2O \Leftrightarrow HB^+ + OH^-$ (proton acceptor)

So Bronsted acid theory is very useful when you are thinking of and dealing w/ weak acids & bases
Ratio of acid & base is where it's @ for buffers

$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$ this is a base.

$NH_4Cl \Leftrightarrow NH_4^+ + Cl^-$

$$\frac{[\overset{x}{NH_4^+}][\overset{x}{OH^-}]}{\underset{2}{NH_3}} = 1.81E-5$$

$NH_3 \rightleftharpoons NH_4^+ + OH^-$

	NH_3	NH_4^+	OH^-
init	2	0	0
Δ	$-x$	x	x
eq	$2-x$	x	x

$$\frac{[NH_4^+][OH^-]}{[NH_3]}$$

~~but~~ so what I really think we have is:

$NH_3 + NH_4Cl + H_2O \rightleftharpoons 2NH_4^+ + OH^- + Cl^-$

	NH_3	NH_4Cl	NH_4^+	OH^-
Init	2	3	0	0
Δ	$-x$	$-x$	$2x$	x
eq	$2-x$	$3-x$	$2x$	x

$$\frac{[2x][x]}{(2-x)(3-x)} = 1.81E-5$$

? $2x^2 - (2-x)(3-x) \cdot 1.81E-5 = 0$

$x = 7.346E-3$

$pOH = -\log(x) = 2.13$

so pH = 11.87

The answer is
9.08
Good Try.

Ok, lets see where we went wrong.

First, we did assume $X = OH^- = NH_4^+$ and this was correct.

The setup for the problem was $$K_b = \frac{\overset{3+x}{[NH_4^+]}\,\overset{x}{[OH^-]}}{\underset{2-x}{NH_3}}$$

Which is what I was going to start out with but then I assumed the Amm. Chloride had an influence on the saturation by creating more NH_4^+. But apparently not.
So the simpler scenario was the right one
Lets see what numbers he uses:

I am going ICE to see if I can see where his numbers came from.

	NH_3	NH_4^+	OH^-
Init	2	3	0
Δ	−x	x	x
Eq	2 − x	3 + x	x

This is his ICE table

Question here!?

Here were our equations: $$\overset{2}{NH_3} + H_2O \rightleftarrows \overset{3???}{NH_4^+} + OH^-$$
$$\underset{3}{NH_4Cl} \rightleftarrows NH_4^+ + Cl^-$$

You do not understand where he initial ICE values came from. You were partly on the right course.

~~Moore~~ Moore's discussion on buffers is rather weak. Let's extend to Schaum or Zumdahl.

SEE ZUMDAHL AHEAD! ALL OK!.

We went to the GRE book next.
It seems to imply that everything you need to know about buffers is contained w/in the HH equation. I hardly think this is the case. They just assume you know the molar concentration of the weak acid & the conjugate base. This is not, I am sure, always the case.

Nevertheless: Important statements from the GRE.

1. HH is undoubtedly very important
2. A buffer must consist of a weak acid & its conjugate base.
3. Buffers are just Le Chatelier's principle applied to acid base equilibrium.
4. Diluting or Concentrating a buffered solution DOES NOT change its pH.
(But it does affect the buffering capacity).

We need to go further.
Let's look @ Schaum.

Schaum's discussion of buffers is also very minimal.

Any pair of weak acid & base can be used to form a buffer solution so long as each can form its conjugate base or acid in aqueous solution.

A buffer contains relatively large amounts of both a weak acid (or weak base) and its strong salt (one that ionizes very well).

If a small amount of a strong acid (or base) is added to a buffer, most of the added H^+ (or OH^-) will combine w/ an equivalent amount of the weak base of the buffer to form the conjugate acid (or base) of that weak base (or acid). The net result is that H^+ or OH^- concentration change very little.

Now lets move to Oregon State: Outline of Book

- Cells, Water and Buffers
  - Energy
    - Structure & Function
      - ~~Catalyst~~ Catalysis
        - Genetic Information
          - Metabolism
            - Signaling
              - Putting it All Together

His chapter on buffer should be quite good.

Ahern's Appendix 2 p 213 w/ notes on each Chapter look especially useful. There is a lot of information packed tightly.

The lower the pK, the stronger the acid.

Weak Acids are written as HA
Strong acids like HCl do not have pka values.

Buffers are generally effective within +/- 1 pka unit of the actual pka.
This is a curiosity; it tells you what acid should be chosen to construct a particular buffer.
Example given of pka of acetic acid as 4.76

pka = -log (Ka) or ~~Ka = pka~~

$\log(Ka) = -pka$
$Ka = 10^{-pka}$ $10^{-4.76} = 1.74E\text{-}5 = Ka$

From table Ka = 1.8E-5 which is close enough.
Therefore, we can see that
pka is a very convenient means of characterizing acids as well as estimating the effective range of a buffer.

What if something has a Ka of 1E-10
then pKa = -log (1E-10) = 10 so this is obviously a very weak acid.
So the exponent of Ka alone gives us a pretty good idea of what the pKa is

For example, Ka for carbonic acid is 4.3E-7
So pKa = -log (4.3E-7) = 6.4 so this suggests a pH of a buffer between 5.4 & 7.4 using carbonic acid. $H_2CO_3 \rightarrow H^+ + HCO_3^-$

At the pKa, it will have equal amounts of HA and A^-.

The term "salt" only refers to the A^-. The "salt" only means that it has lost a proton. The difference between an acid and a "salt" is a single proton.

A buffer will be at its maximum capacity when the pH = pKa. We can see, therefore, that the pKa is a very important number.

A main value of HH equation is that if we know the pKa we can predict the ratio of "salt" to acid as a function of pH. (ie, negative to positive charge ratio)

* Consequently we can predict the charge on amino acids in a protein as the pH changes. This is most likely a monumental benefit.

Small pH changes make a very big difference!

A lot is really on focus here.

HH lets us predict the charge of a molecule in solution if we know the pH & pKa of the molecule in solution.

[redacted]

@ p216 Ahern

Rule of Thumb:

(this means + charge)

If the pH ≤ pKa − 1 the proton is <u>on</u> it.

If the pH ≥ pKa + 1 the proton is <u>OFF</u> it.

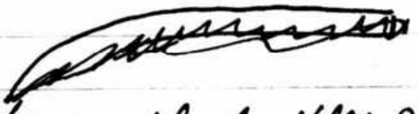
The rule of thumb is valuable for estimating charge. Determination of the pH where the charge is zero requires calculation.

Some examples of this will be very useful. Let's look @ Ahern's text in more detail.

HH: $pH = pKa + \log\left(\frac{A^-}{HA}\right)$ $\left(\frac{\text{base}}{\text{acid}}\right)$

It would be good to get a graph of this equation but I am not succeeding well yet

The surface graph seems to be of the form



looking edge on. is a very gradual addition to the pKa term which makes sense from a log function.

Changing charges on biological molecules, esp proteins, can drastically affect how they work and even whether they work @ all.

Page 132

	pK
Oxalic acid is a very "strong" weak acid.	1.23/4.2
Carbonic acid is a very "weak" weak acid	6.3/10.2
Phosphoric acid (3) is even weaker	2.1/12.4
Acetic acid is pretty much in the middle	4.8

One definition for an acid is just that the protons can come off (dissociate) when dissolved in water.

When you dissolve HCl in water, it is no longer "HCl" It is now H^+ and Cl^- as it completely dissociates.

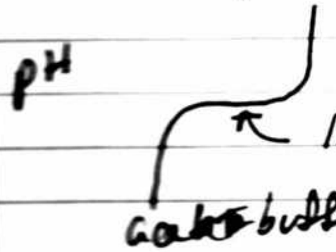
Ahern is on to what we need to know.

He makes an analogy of weak acids to that of a battery - always being able to provide protons when needed. He likens it to a UPS
Uninterruptible Power Supply, like a laptop battery.
With acetic acid, about 4 in 1000 HAc's come apart.

The UN dissociated HAc acts as a backup supply for more H^+.

A buffer works by having the weak acid release more protons to compensate for those that are "used up" in reacting w/ the OH^- ions.

The HH equation predicts this response.



a buffer pH graph is like this.
In this zone it is resisting change

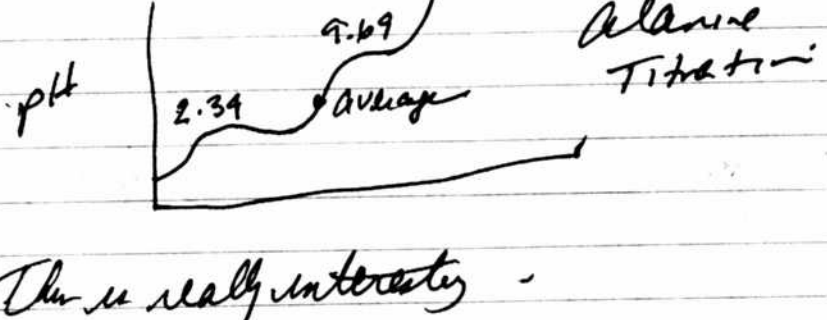
Why We Care About Buffers

An eg of why a buffer is important.

When you exercise, you produce protons. If your blood did not have a buffer, your blood would acidify, and you would die because proteins in the blood would become denatured or deactivated.

A flattened section in a titration curve is indicative of a buffering region.

Now he is starting to talk about predicting charge on an amino acid as a function of pH. This is where things get real interesting real quickly.

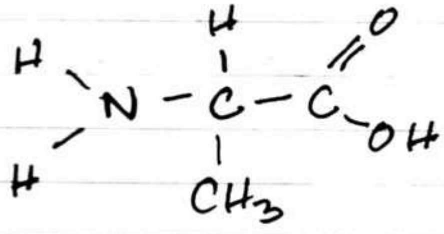


This is really interesting.

So let's look into alanine more closely.

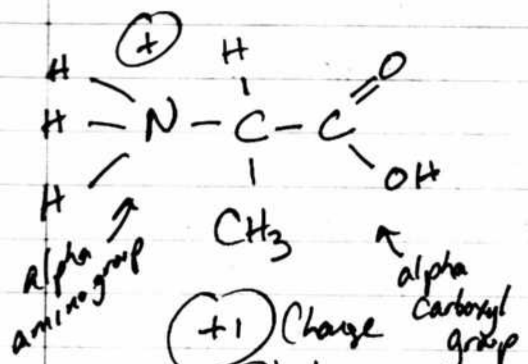
So if pH < 1.34 then proton is ON for the amino group.
if pH > 9.69 then proton is OFF for the carboxyl group.
if pH > 5.01 & < 7.01 then it is probably neutral with a proton ON for the amino group and OFF for the carboxyl group.

Alanine structure



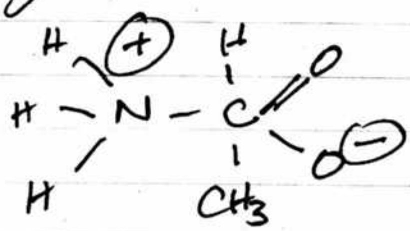
so the R group is a methyl group

Allen given three states for alanine



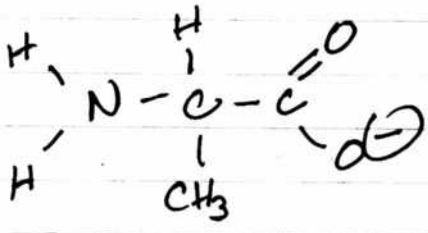
(+1) Charge State

Proton ON



0 charge State

pI = 2.34
+ 9.69
/2 = 6.01
pH of neutral charge



Proton OFF

Negative Charge State
(−1)

So we are seeing that hydrogen can come and go and that this induces change.

So we can see that a titration may well be able to define a protein.

Now we are starting to get somewhere.
We certainly see the value of the pKa.
We also see that maybe titration can be used to define a problem. That is a very ~~literally~~ topic.

We are getting closer to investigating a buffer in Chem Lab.
Ahern has taught us a lot about the ~~practicality~~ and importance of buffers.

Now we go to Zumdahl.
The common ion effect has now been defined and there is one thing that I was exactly concerned about, ie what the effect of

$HF + NaF + \cancel{H_2O} \underset{H_2O}{\rightleftharpoons} H^+ + F^- + Na^+ + F^-$

and there is the additional influence from the fluoride salt.
Zumdahl is really going to cover these topics in sufficient detail.

We have a great of practical problem on p 715 that introduces quantitatively the common ion effect.

Given: A solution containing 1.0M HF (Ka= 7.2E-4) <u>and</u> 1.0M NaF.

This is great. It is somewhat like the problem I had earlier from Moore that I never did resolve correctly.

So we know we have

$$HF + NaF \xrightleftharpoons{H_2O} H^+ + F^- + Na^+ + F^-$$

Now we know that the extra F^- shifts the reaction to the left.

Na^+ is neither acidic or basic, so it is like a spectator ion: water is also not relevant.
So our only important species are HF, H^+ & F^-.
We can now say that

$$\frac{[H^+][F^-]}{[HF]} = 7.2E-4$$

So now the question is, what are the concentrations of H^+ & F^-
I like ICE tables:

	HF	H^+	F^-	
init	1.0	0	1.0	(because the NaF dissolves immediately!)
Δ	−x	x	x	This is great
eq	1−x	x	1+x	

So $$\frac{x(1+x)}{1-x} = 7.2E-4$$

$\sim x(1+x) - (1-x)7.2E-4 = 0$ $x = 7.2E-4$!!

This is correct and notice it can be the same as Ka.
I would never have expected that is possible

I understand this explanation completely.

$pH = -\log(7.2E-4) = 3.14$

% of Dissociation = $\frac{7.2E-4\,M}{1.0M}$ = .072 %

I like this style & interpretation also.

I just bet, with this superior presentation by Zumdahl on p 716 that we can now work the problem that was so inadequately presented by Moore.
Let's recall that problem:

Given: 2 moles of Ammonia (NH_3)
3 moles of Ammonium Chloride NH_4Cl
1 liter of solution
$K_b = 1.81E-5$

Question: - What is the pH?

We know

this dissociates $H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$

this ionizes fully $NH_4Cl \rightarrow NH_4^+ + Cl^-$

so

$NH_3 + NH_4Cl + H_2O \leftrightarrow NH_4^+ + OH^- + NH_4^+ + Cl^-$

Now, what is important as far as acid-base?
Cl^- is not, water is not
Excess NH_4^+ shifts equilibrium to left
OH^- is very important as base so

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

So our ice table will be

this dissociates

because it ionizes completely and immediately

	NH_3	NH_4^+	OH^-
init	2	3	0
Δ	$-x$	x	x
g	$2-x$	$3+x$	x

so $\frac{(3+x)(x)}{2-x} = 1.81E\text{-}5$

or $(3+x)(x) - 1.81E\text{-}5(2-x) = 0$

$x = 1.207E\text{-}5$

$pOH = -\log(1.207E\text{-}5)$

$pOH = 4.92$

a $pH = 9.08$

Which is exactly the right answer.

Zumdahl made this straight forward & enjoyable. More obscured the essential information and made the problem much more difficult and frustrating & did not emphasize the immediacy of full ionization of the "salt".

Even now, we understand how we are ready to proceed w/ Zumdahl's Buffer section.

[redacted]

Dec 24 2015 Christmas Eve
Zumdahl Buffers

A buffer solution may containing (but apparently not always) a weak acid and a Common ion salt. ~~The common ion salt~~

Yes, here it is again. Buffered solution are simply solution of weak acids or bases containing a common ion.. This is not a new type of problem! Zumdahl is going to give us everything we need, including preparing a buffer.

1st Problem: pH of a buffered solution

Given 0.50M Acetic Acid $C_2H_4O_2$
0.50M Sodium Acetate Na[illegible]$C_2H_3O_2$
$K_a = 1.8E{-5}$

We know that:

dissoc. $C_2H_4O_2 \overset{H_2O}{\rightleftarrows} C_2H_3O_2^- + H^+$

ionizable $NaC_2H_3O_2 \xrightarrow{H_2O} Na^+ + C_2H_3O_2^-$ (common ion)

So
$C_2H_4O_2 + NaC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^- + Na^+$

Who is not important?
Na^+
$Na_2C_2H_3O_2$

Therefore our ICE table should be:

	$C_2H_4O_2$	H^+	$C_2H_3O_2^-$
Init	0.5M	0	0.5M (from ionization)
Δ	$-x$	x	x
Eq	$.5-x$	x	$.5+x$

Prepare then: $\frac{(x)(.5+x)}{(.5-x)} = 1.8E-5$

or $x(.5+x) - 1.8E-5(.5-x) = 0$

$x = 1.8E-5$

$pH = -\log(1.8E-5) = 4.74$

GOOD JOB!
GOOD WORK!

Now we have a new situation to analyze.
Now we are going to add NaOH to a buffer to see how it behaves.
Given: 0.01M NaOH (solid) is added to 1.0 liters of the buffer that contains: the ingredients of the previous problem that we just solved.
Compare this change when the same NaOH (solid) is added to water.
Lets do water first

$$NaOH + H_2O \rightarrow Na^+ + OH^-$$

0.01M 0.01M 0.01M

$pOH = -\log[OH^-] = -\log[.01] = 2$

$pH = 14 - 2 = \underline{10}$

Now, let's think what happen when we add it to the buffer.

Given that we have
$(.5-1.8E-5M)\ C_2H_4O_2$
$1.8E-5\ H^+$
$(.5+1.8E-5M)\ C_2H_3O_2^-$
with a pH of 4.74
and a K_a of 1.8E-5

What happen when we add 0.01 M NaOH
well, let's assume we have one liter of solution.

$NaOH \rightarrow Na^+ + OH^-$

so
$C_2H_4O_2 + NaOH \rightleftarrows H^+ + C_2H_3O_2^- + Na^+ + OH^-$
who is not important: Na^+ & NaOH, so we have

	$C_2H_4O_2$	H^+	$C_2H_3O_2^-$	OH^-
init	(.5-1.8E-5)	(1.8E-5)	(.5+1.8E-5)	0
Δ	0	~~1.8E-5~~-x	0	.01
eq	.5-1.8E-5	0 1.8E-5-x	.5+1.8E-5	.01

We also know $k_w = k_a \cdot k_s$ n $k_s = \frac{1E-14}{1.8E5} = 5.5E-10$
So we have

$$\frac{\cancel{(.5+1.8E-5)}(.01)}{\cancel{(.5-1.8E-5)}} = \frac{(.01)(1.8E-5-x)}{(.5-1.8E-5)} = 5.5E-10$$

$x = 1.79E-5$
$pOH = -\log(1.79E-5) \approx 4.75$
They got 4.76. I seem to be on the right track

Page 142

But I also thought that I have a problem. And I need to review this one further. By my logic my pH is actually $14 - 4.75 = 9.25$ which is quite wrong. So let's review.

We actually need two ICE tables. One for ~~equil~~ stoichometry & one for equilibrium. Ok, I am seeing the [illegible] now. You missed a very important aspect of the problem. The stoichometry ICE table is as follows

First we had the overall reaction correct

$$C_2H_4O_2 + NaOH \rightleftharpoons H^+ + C_2H_3O_2^- + Na^+ + OH^-$$

but, and an important but, is that the OH^- SHIFTS the reaction to the left

Remember!

This means that the actual reaction of interest is now

$$OH^- + C_2H_4O_2 \rightarrow H_2O + C_2H_3O_2^-$$

This is a really important interpretation. Even the H^+ is so small that it is not considered a major species of the reaction.

We can set up an ICE for this as

	OH^-	$C_2H_4O_2$	$C_2H_3O_2^-$
Init	.01	0.5M	0.5M
Δ	−.01	−.01	+.01
Eq	0	.49M	.51M

Stoichometry ICE - Full Ionization

Next he goes to the equilibrium portion of the reaction, ie dissociation, and now the NaOH is no longer a part of the problem.

Now it is simply

$$C_2H_4O_2 \rightleftarrows H^+ + C_2H_3O_2^-$$

and ICE for this is:

	$C_2H_4O_2$	H^+	$C_2H_3O_2^-$
Init	.49M	0	0.51M
Δ	$-x$	x	x
eq	$.49-x$	x	$.51+x$

and $K_a = 1.8E-5$

so

$$\frac{(x)(.51+x)}{(.49-x)} = 1.8E-5$$

or

$$x(.51+x) - 1.8E-5\,(.49-x) = 0$$

$x = 1.729E-5$

pH = $-\log(1.729E-5) = 4.76$

Compared to 4.74

So this was an excellent example of how a buffer works. You are showing mathematically that adding OH$^-$ to a buffer is an entirely different process than adding OH$^-$ to water.

It is basically because of Le Chatelier's Principle that this happens. Adding OH$^-$ to the buffer shifts the reaction to the left and actually results in an equation w/ OH$^-$ on the reactant side, which is very interesting in its own right.

We also see that adding OH$^-$ to a buffer is best handled in two parts. First, the part that ionizes completely to begin with, what Zumdahl calls the stoichiometry portion. Then secondly, handle the equilibrium portion.

These problems are very interesting and I think are quite practical. The last example is essentially how blood behaves.

Even tho we have shown by example that a buffer does work, Zumdahl asks the ever important question for understanding, i.e., How does it work?

Dec 25 2015 Zumdahl

When you have a buffer and add OH^- you create the following scenario:

this is dissociation

$HA \rightarrow H^+ + A^-$ (and then add OH^-)

goes to

adding these — replaces with this

$OH^- + HA \rightarrow A^- + H_2O$

Then in the shift to the left per Le Chatalier's Principle.

The net result is that OH^- ions are "not allowed" to accumulate but are replaced by A^- ions.

there are two processes that you need to know here

what is this called?

$OH^- + HA \rightarrow A^- + H_2O$

so this does split, and since H becomes H^+ A must become A^-

PM Monitoring Dec 25 2015

We have enough data now to start looking @ PM as a function of wind & population.

	y PM	Pop	x Wind
3	2	0	3
4	2	0	2
5	2	0	10
6	13	0	22
7	13	2	3
8	2	0	2
9	2	0	5
10	2	0	8
11	2	0	4
12	2	0	15
13	25	0	15
14	10	2	10
15	5	1	15
16	20	0	20
~~17~~			

$PM = .65(\text{Wind}) + 1.0$

$r = .58$

$r^2 = .33$

Wind	PM
0	1
5	4
10	8
15	11
20	14
30	20
40	27

$PM \cong 2.02(\text{POP}) + 6.5$ $r^2 \cong .04$

Initial Model

Population	PM
0	6.5
1	8
2	~~12~~ 10
3	12
4	14

So

$$PM \cong \left[(.65(\text{Wind}) + 1.0)^2 + (2.02(\text{POP}) + 6.5)^2 \right]^{1/2}$$

Wind = 20
Pop = 3

196   158

$PM \cong 18.8$ ok

Back to the Buffer situation with Zumdahl

This seems to be the heart of why a buffer is effective: Zumdahl p720:

" If the amounts of HA and A^- originally present are very <u>large</u> compared w/ the amount of ^-OH added, the change in the [HA/A^-] ratio will be small"

" The essence of buffering then, is that [HA] and [A^-] are large compared with the amount of OH^- added."

We now continue to work problems; this is how we actually learn what's happening.

Given:

0.15M lactic acid $C_3H_6O_3$
0,25M Sodium lactate $NaC_3H_5O_3$??
$K_a = 1.4E{-4}$

I would like the formula for sodium lactate
$C_3H_5NaO_3$ Yes so you have it right. good.

Our proposed reactions are therefore:

$C_3H_6O_3 \rightleftharpoons C_3H_5O_3^- + H^+$ dissoc.

$NaC_3H_5O_3 \rightarrow Na^+ + C_3H_5O_3^-$ ionizable

what is involved in acid-base?

$C_3H_6O_3 \rightleftharpoons H^+ + C_3H_5O_3^-$ Salt & Na^+ are not

Let's go after pH, ICE table

	$C_3H_6O_3$	H^+	$C_3H_5O_3^-$	
init	.75M	0	.25M	starting
Δ	−x	x	x	dissociates
Eq	.75−x	x	.25+x	net

so $\frac{(x)(.25+x)}{(.75-x)} = 1.4E-4$

$x = 4.191E-4$

$pH = -\log(4.191E-4) = 3.38$ perfect

you are doing very well with these.

You are now getting more proficient @ determining the pH of a buffer! This is a great accomplishment.

The reason that it would be so important to understand the effect of adding a strong base or acid to a buffer is that it will definitely be involved in any titration methods that are used or developed.

0 <100
1 <1000
2 <10,000
3 <100,000
4 500,000+

PM Monitoring

mem Date Location, State - WX
Time Pop ~~WX~~ Vis Traffic PM T° Wind, Dir %RH Elev Vis

12-26 TR Camp, Smoky Campfire
PM 50 - 300 !!!

13 12-27 TR Camp Cldy, Stratus
1915 0 None Vis. 2 14°C 8 fmW 15% 5500 60.

mem 14 12-28 TR Camp, Clear
1515 0 None 2 10° 4 fmW 30% 5500 80+
(12-29 Moving Day)

mem 15 12-30 Lordsburg NM Clear
0930 1 None 2 16°C 01-S 21% 4600' ~~60+~~ 70

indoor 16 12-30 Benson Denny's Restaurant
1200 35 32°C 6% 4600'

17 12-30 Tucson (Collosal Cave Camp) Partly Cloudy - nite Cirro-Stratus
2245 0 None 2 11°C 1-W 25% 2700' 50

18 12-31 Tucson (Collosal Cave) Partly Cloudy - Cirro Stratus
0845 0 None 2 8°C 1-NE 34% 2700' ~~50~~ 40

~~12-31 Tucson (Collosal Cave) - Partial Aerosol~~ Banks
~~Some light traffic did appear~~, Visibility is
~~diminished~~
~~12-31 0 Light~~ Traffic ~~today~~
~~1545~~ 0 Traffic: light (1)
~~Third~~ Day

Page 150

PM 2.5 #2

Some Wave Formations (AltoCumulus)

Mem ✓ 12-31-15 Tucson (Collosal Cave) Light Aerosol, Linear-Banks Potential, Photo Taken
Mostly Sunny
19 1600 0 Light Traffic (1) 2 19°C 2-W 16% 2700 40

✓ 01-01-16 Tucson ~~(Collosal~~ Cave) Clear
20 1200 0 None 2 ~~5~~ 23°C ~~SE~~ 5-SE 21% 2700 60

21 ✓ 01-02-16 Tucson (Collosal Cave) Clear
2115 0 None 2 16°C 4-~~N~~NE 30% 2700 60

22 ✓ 01-03-16 Tucson (Collosal Cave) Clear
Photo taken 0900 0 None 2 12°C 6-SE 40% ~~2700~~ 3700' 60

Indoor 23 ✓ 01-03-16 Tucson (Indoor Camper) (Collosal Cave)
Photo 0915 0 20 23°C 38%

01-04-15 Trip to Phoenix, Rain
24 ✓ 01-05-16 Tucson (Collosal Cave) Clear
1115 0 None 2 21°C 01-N 31% 3700' 70

25 ✓ 01-06-16 Tucson (Collosal Cave) Clear
2200 0 None 2 7°C 01-W 62% 3700 70

01-07-16 Travel to Phoenix to Pick up Trailer

✓ 01-08-16 Casa Grande (midway between Tucson & Phoenix) Mostly Cldy
0830 1 None 2 7°C 04-S 75% 3000' 50

Indoor ✓ 01-08-16 Tucson ~~(Collosal Cave) Clear~~ Terry RV Reading
28 1945 0 14 24°C 40%

29 01-09-16 Tucson (Collosal Cave) Clear
1500 0 None 2 22°C 01-N 18% 3700' 70 ft m

Projects ahead are
1. Citizen Science Alliance
2. PM2.5 R file analysis
[redacted]

On we go to another buffer, this one a <u>base</u>.

Given:
$0.25M\ NH_3$ $K_b = 1.8E-5$
$0.40M\ NH_4Cl$

Problem: Determine the pH.
This involves a weak base. My proposed reactions are

diss. $H_2O + NH_3 \rightleftarrows NH_4^+ + OH^-$ 5H, 1O, 1N Balanced
ionizes $NH_4Cl\ (+H_2O) \rightarrow NH_4^+ + Cl^-$

What is involved in acid-base: NH_3, NH_4^+, OH^-
so the net reaction involved should be:

$$NH_3 \rightleftarrows NH_4^+ + OH^-$$

and ice table:

	NH_3	NH_4^+	OH^-
Init	.25M	.40M	0
Δ	$-x$	x	x
eq	$.25-x$	$.40+x$	x

or $$\frac{(.40+x)(x)}{(.25-x)} = 1.8E-5$$

$x = 1.125E-5$

$pOH = -\log(1.125E-5) = 4.95$

$pH = 14 - 4.95 = \underline{\underline{9.05}}$ perfect.

Excellent work is taking place here.
I am now successfully predicting the
pH of a buffer.

Adding an acid or a base to a Buffer - major principles

* Important Section

OK, here we go. Adding a strong acid to a buffer (We have added NaOH one time and learned several tricks).

Given: The previous buffered solution.
We add 0.10 moles gaseous HCl to 1.0 liters of the buffer.

It is 0.1 M HCl!

Problem: What is the pH?
We have learned that we take care of stoichometry first.
But we must define the reaction, this is ever crucial.
Before, we learned that if we add NaOH we essentially take

$$HA \rightleftarrows H^+ + A^-$$

and transform the situation to:

$$OH^- + HA \rightleftarrows A^- + H_2O$$

This changes everything, and involves stoichometry before we deal w/ the equilibrium.

We are now learning that there are two sides to this picture

Either (adding acid to a buffer)

(think $H_2O + NH_3$) base think NH_4^+

adding acid to a buffer

$$HA \rightleftarrows H^+ + A^- \qquad H^+ + B \rightleftarrows BH^+$$

acid

and or and

adding acid to a buffer

adding OH to a buffer

$$OH^- + HA \rightleftarrows A^- + H_2O \qquad OH^- + BH^+ \rightleftarrows B + H_2O$$

(adding OH to a buffer) (adding OH to a buffer)

This is a very important summary of the adding strong acid or base to a buffer solution.

Now that we have this important table, lets see if we can apply it to our problem.

Lets recall the net equation for our buffered solution:

$$NH_3 \leftrightarrows NH_4^+ + OH^-$$

it is 0.1M HCl!

(combined dissociation & ionized salt)

Now to this we add 0.1 ~~1.0~~ M HCl (a strong acid) and we know to take care of stoichiometry first.

Our problem is as follows:

$$H^+ + B \leftrightarrows BH^+$$

notice the similarity of this to our original dissociation

– the difference is that we are adding $\underline{\underline{H^+}}$ directly (from HCl) NOT H_2O!

This means that we now have a situation of

$$H^+ + NH_3 \leftrightarrows NH_4^+$$

But we must take care of the stoichiometry first.

ICE for stoichiometry:

	H^+	NH_3	NH_4^+
init	0	0.25M	.40M
Δ	.1M	−.1M	+.1
eq	.1M	~~0.24M~~ 0.15M	0.50M

Now we should be able to work on the equilibrium situation:

	NH_3	NH_4^+	OH^-
init	0.15M	0.50M	0
Δ	−x	x	x
eq	.15−x	.50−x	x

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This now leads to:

$$\frac{(.50-x)(x)}{(.15-x)} = 1.8E-5$$

or $x = 5.40 E-6$

$pOH = -\log(5.40 E-6) = 5.27$

and

$pH = 14 - 5.27 = \underline{\underline{8.73}}$ Perfect a Mundo!

(It used to be 9.05
quite remarkable how
stable the buffer is)

Great Job Clifford.
This was a very good solution.
Your table in pink is indispensable
on the previous page.

Buffering Capacity:

We can surmise more intuitively where the problem was headed and it may not be necessary to execute it. It is similar to the previous problem. The upshot of it is:

For maximum buffering capacity, the pKa of the weak acid to be used in the buffer should be as close as desired to the desired pH.

This is what guides the construction of a buffer. It also demonstrates the motive for creating a synthetic acid and a synthetic base. Buffer constituents of electrophoresis

Now for the Granddaddy Prize of all as far as I am Concerned.

The Preparating a Buffer problem! p 728 Zumdahl

We want the buffer effective @ a pH of 4.30.
We have 4 acids to choose from.
Lets solve for the pka:

	ka:	pka	
	1.35E-3	2.87	
	1.3E-5	4.89	
Benzoic Acid	6.4E-5	4.19	← This would clearly seem to be the best
	3.5E-8	7.45	

pka = -log (ka)

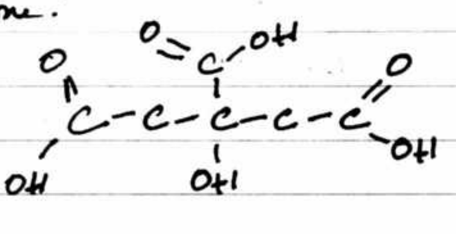
We are absolutely correct, simply & rightfully so.

Another method is to use a variation of the HH equation, but that is hardly necessary if you simply understand the relation

pka = -log (ka)

And that puts us, for the first time, w/ a preliminary grounding in acid-base Chemistry along w/ buffer performance, titration, and buffer construction.

Very soon now we are headed toward the simulator. But before we do so, it make you wonder about how you made a buffer of citric acid & baking soda? Let's see what you might have done?

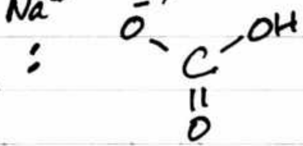


Citric Acid Formula: $C_6H_8O_7$

Baking Soda Formula: $NaHCO_3$

Also an interesting question: What are good buffers around pH 7.0?

$NaHCO_3$:



There are 3 or 4 dissociations of citric acid. No wonder it can find a way to share w/ the carbonate ion. But it is not a simple buffer to compute. Tripotic Acid

So the buffer is not nearly so simple as acetic acid. The DIY book may cover this better.

pKa's for citric acid are 3.13
4.76
6.40 $Ka_1 = 7.4E-4$

Many microbial cultures are buffered w/ citric acid over a pH range of 2.5 to 7.0 because of the above pKa values.

It is the hydrogen that comes off @ the highest pH that would contribute the most @ a pH of 6.8. What salt is used? Calcium Citrate is one example

Blood buffer contains Carbonic acid
and bicarbonate. pH 7.4

Carbonic Acid H_2CO_3
bicarbonate HCO_3^-

~~Buffered~~
Buffered aspirin is another example

—

Di Sodium
Citric Acid - Phosphate Buffer
Na_2HPO_4

pH 7.0 uses 82.35 ml of 0.2M Na_2HPO_4
17.65 ml of 0.1M Citric Acid

Sodium Citrate buffer can be made using
Citric Acid & trisodium citrate.

Why not citric acid & calcium citrate?
or sodium citrate.

tri ~~(mono)~~ Sodium Citrate $Na_3C_6H_5O_7$
mono $NaC_6H_7O_7$ - first hydrogen all hea
di $Na_2C_6H_6O_7$

Trying to Identify pKa for a Complete unknown.

Everyday investigations has many interesting propositions.

One of them is the prospect of

How would you go about determining the identity of certain acids that are in soft drinks, for example.

Such as:	Ka_1	Ka_2	Ka_3
Phosphoric Acid	7.8E-3	etc	
Citric Acid	7.4E-4		
Oxalic Acid	6.5E-2		

So, after all the studying that you have done, how would you go about this? Titrate w/ NaOH? How exactly?

We know that $HA \leftrightarrow H^+ + A^-$ and that $\frac{[H^+][A^-]}{HA} = Ka$

Here we go

So Given unknown
We have HA of .X M concentration We also know the initial pH.
We titrate it w/ 0.1 M NaOH
25 ml of NaOH and the equivalent point reached @ ~ 8.4
What is the Ka of the acid?

This is a very interesting problem, isn't it and the real world.

Let's think about this, Recall our problem of the equivalence point. This is not a buffer problem, it is a titration problem.

The first step would be to titrate the acid and look @ the titration curve. The equilibrium point and shape of the titration curve ~~wor~~ will let us know if it be a strong acid or a weak acid. It is much more likely to be a weak acid.

So let's assume we determine that it is a weak acid, and we measure the initial pH at 3.8

Lets go back to how we determined the pH of a weak acid. We are also going to need the original volume. Let's say it is 100 ml of the weak acid.

$$HA \rightarrow H^+ + A^-$$

We know fm that

$$\frac{[H^+][A^-]}{HA} = Ka$$

this assumes 1:1 molar concentration

pKa ~~pH~~ ~~$= -\log(Ka)$~~

~~so $\log(Ka) = -pH$~~

~~$Ka = 10^{-pH}$~~

~~so $\frac{[H^+] + [A^-]}{[HA]} = 10^{-pH}$~~

but we also know that $pH = -\log[H^+]$

but

~~This means $\frac{x^2}{[HA]} = 10^{-3.8}$~~

~~$x^2 = [HA] \cdot 1.58E-4$~~

Try to identify pKa
of an unknown

so $3.8 = -\log[H^+]$ ∴ $\log[H^+] = -3.8$

so $[H^+] = 10^{-3.8} = 1.58E-4$
So we do know something about the original nature
of the unknown acid. But this is all we know.

But now let's say we add 10 ml ~~0.1M~~ 0.01 NaOH and the pH
change to 4.6. Now what do we know?

$HA \rightarrow H^+ + A^-$ diss. and we know $[H^+]$
$NaOH \rightarrow Na^+ + OH^-$ ionizes completely
Now, when we add a strong base to a weak acid
it changes everything, and it messes our tables.
But remember, this is not a buffer problem!!!!

If we use 10 ml of .01 NaOH we have $\frac{\cancel{0.1}\ 0.01 \text{ moles}}{1000 \text{ ml}}$ 10 ml = ~~1E-3~~ 1E-4 moles NaOH

We do know now that we will neutralize ~~1E-3~~ 1E-4 moles of the weak acid.

I think that you have overlooked the ICE development
on page CW#1 (Chemwiki#1) OK, you were right,
The actual set up is the same result.

~~H H+~~ $HA \rightarrow H^+ + A^-$

means

	HA	H^+	A^-	$\frac{X^2}{Z-X}$
Init	ZM	0	0	
Δ	-x	X	X	
eq	Z-x	X	X	

$pH = -\log[H^+]$; $H^+ = x$, so
$3.8 = -\log[x]$ $\log(x) = -3.8$ $X = 10^{-3.8} = 1.58E-4$ OK ✓

Pop
0 <100
1 <1000
2 <10,000
3 <100,000
4 500,000+

PM Monitoring

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mem Date Location, State - WX
Time Pop ~~WX~~ Vis Traffic PM T° Wind, Dir %RH Elev Vis

12-26 TR Camp, Smoky Campfire
PM 50 - 300 !!!

13 12-27 TR Camp Cldy, Stratus
1915 0 None Vis. 2 14°C 8 fm W 15% 5500 60.

mem 14 12-28 TR Camp, Clear
1515 0 None 2 10° 4 fm W 30% 5500 80+
(12-29 Moving Day)

mem 15 1230 Lordsburg NM Clear
0930 1 None 2 16°C 01-S 21% 4600' ~~68+~~ 78

Indoor 16 12-30 Benson Denny's Restaurant
1200 35 32°C 6% 4600'

17 12-30 Tusson (Collosal Cave Camp) Partly Cloudy - nite Cirro-Stratus
2245 0 None 2 11°C 1-W 25% 2700' 50

18 12-31 Tucson (Collosal Cave) Partly Cloudy - Cirro Stratus
0845 0 None 2 8°C 1-NE 34% 2700' ~~50~~ 40

~~12-31 Tucson (Collosal Cave) - Partial Aerosol~~ Banks
~~Some light traffic did appear, Visibility~~ is
~~diminished~~
~~12-31 0 Light today~~ Traffic
~~1545~~ 0 Traffic: Light (1)
~~that~~ Day

Adding an acid or a base to a Buffer - major principles

* Important Section

OK, here we go. Adding a strong acid to a buffer (We have added NaOH one time and learned several tricks).

It is 0.1 M HCl!

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We add 0.10 moles gaseous HCl to 1.0 liters of the buffer.
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$$HA \rightleftarrows H^+ + A^-$$

and transform the situation to:

$$OH^- + HA \rightleftarrows A^- + H_2O$$

This changes everything, and involves stoichiometry before we deal w/ the equilibrium.

We are now learning that there are two sides to this picture

adding acid to a buffer	Either (adding acid to a buffer) $\underset{\text{acid}}{HA} \rightleftarrows H^+ + A^-$	or	(think $H_2O + NH_3$) think NH_4^+ $H^+ + \overset{\text{base}}{B^*} \rightleftarrows BH^+$ (adding acid to a buffer)
	and		and
adding OH to a buffer	$OH^- + HA \rightleftarrows A^- + H_2O$ (adding OH to a buffer)		$OH^- + BH^+ \rightleftarrows B + H_2O$ (adding OH to a buffer)

This is a very important summary of the adding strong acid or base to a buffer solution.

Now that we have this important table, lets see if we can apply it to our problem.

This now leads to:

$$\frac{(.50-x)(x)}{(.15-x)} = 1.8E\text{-}5$$

or $x = 5.40\ E\text{-}6$

$pOH = -\log(5.40\ E\text{-}6) = 5.27$

and

$pH = 14 - 5.27 = \underline{\underline{8.73}}$ Perfect a Mundo!

(It used to be 9.05 quite remarkable how stable the buffer is)

Great Job Clifford.

This was a very good solution.

Your table in pink is indispensable on the previous page.

Buffering Capacity:

We can surmise more intuitively when the problem was loaded and it may not be necessary to execute it. It is similar to the previous problem. The upshot of it is:

For maximum buffering capacity, the pKa of the weak acid to be used in the buffer should be as close as desired to the desired pH.

This is what guides the construction of a buffer. It also demonstrates the motive for creating a synthetic acid and a synthetic base buffer combination, of electrophoresis.

LOG Differential

CW#2 (Chemwiki #2

There are probably two ways that we
Can proceed with adding a "little NaOH"
ICE or HH
They should likely both work.

Now the HH method is

$$pH = pKa - \log\left(\frac{[HA]}{[A^-]}\right) \quad \text{or} \quad pH = pKa - \log(R_i)$$

It would be of interest to look @ this from a differential point of view

$$dpH = 0 -$$

So $\ln(x) = \ln(10) \cdot \log(x)$
$\ln(x) = 2.303 \cdot \log(x)$

$$\frac{d(\log x)}{dx} = \frac{1}{x \cdot \ln(10)} \qquad \frac{d[\ln(x)]}{dx} = \frac{1}{x}$$

$$\log(x) = \frac{\ln(x)}{\ln(10)} \qquad \frac{d(\log(x))}{dx} = \frac{1}{x \cdot \ln(10)}$$

so $$\frac{d(\cancel{d}\log(x))}{dx} = \frac{1}{2.303 \cdot x}$$

Now, in this case X is the ratio of acid to base,

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LOG RULES

Here is what we know

init $3.8 = pka - \log(R_1)$

Δ_1 $4.6 = pka - \log(R_2)$

If we subtract these we know that

$0.8 = -\log(R_2) + \log(R_1)$

so now we know that

$0.8 = \log(R_2^{-1} \cdot R_1)$

$0.8 = \log\left(\frac{R_1}{R_2}\right)$

$0.8 = \log\left(\frac{R_1\ (\text{init})}{R_2\ (\Delta_1}\right)$

what is $\log(a) + \log(b)$?

$\log(5) + \log(3) =$
$.699 + .477 = 1.176$

$\log(x) + \log(y) = \log(xy)$

? $c \cdot \log(x) + d \cdot \log(y) = \log(x^c \cdot y^d)$

yes.

so $-\log(5) + \log(3) = \log\left(\frac{3}{5}\right)$

$-1 \cdot \log(5) + 1\,(\log(3)) = \log(5^{-1} \cdot 3^1)$

$= \log\left(\frac{3}{5}\right) = -.22$

Now, what do we know about R_1 & R_2?

Well, initially, as for the ice table, the $R_1 = \frac{Zm}{0}$ which is ∞, so this does not seem to help.

@ $R_2 = \frac{Z_m - x}{x}$

but hold on, we know H^+ I believe @ both R_1 & R_2

$pH = -\log[H^+] \Rightarrow H^+ = 10^{-4.8} =$ ~~1.58E-5~~ 2.51E-5

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Now, if we assume equal mole dissociation.
Then means that $[A^-] = [H^+]$

This mean that we know that

$$0.8 = \log\left(\frac{\dfrac{HA_1}{1.58E-4}}{\dfrac{HA_2}{2.51E-5}}\right) = \log\left(\frac{R_1}{R_2}\right)$$

or

$$0.8 = \log\left(\frac{HA_1}{1.58E-4} \cdot \frac{2.51E-5}{HA_2}\right)$$

or

$$0.8 = \log\left(0.159 \frac{HA_1}{HA_2}\right)$$

Now we know that $\log\left(\frac{x}{y}\right) = \log x - \log y$

but also

$$10^{0.8} = \frac{.159\, HA_1}{HA_2}$$

or $\frac{HA_1}{HA_2} = \underline{\underline{39.68}}$ This means HA_2 is 0.025 the concentration of HA_1

This looks like pretty good deductive work.

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Now, what if we add the equations:

$8.4 = 2pka - \log(R_1) - \log(R_2)$

$8.4 = 2pka - 1(\log(R_1) + \log(R_2))$ but we know $\log(x) + \log(y) = \log(xy)$

so

$8.4 = 2pka - 1 \cdot \log(R_1 \cdot R_2)$

$8.4 - 2pka = -\log(R_1 \cdot R_2)$

$\log(R_1 \cdot R_2) = 2pka - 8.4$

$R_1 \cdot R_2 = 10^{(2pka - 8.4)}$

$R_1 \cdot R_2 = 10^{2pka} \cdot 10^{-8.4}$ $\qquad 10^{-8.4} = 3.98E-9 \overset{\sim}{=} 0$

so we have

$R_1 \cdot R_2 \overset{\sim}{=} 10^{2pka} \cdot 3.98E-9$

~

$\frac{HA_1}{1.58E-4} \cdot \frac{HA_2}{2.51E-5} = 10^{2pka} \cdot 3.98E-9$ ~ $HA_1 \cdot HA_2 = 10^{2pka} \cdot 3.96E-9$

~

$\frac{HA_1 \cdot HA_2}{3.96E-9} = 10^{2pka} \cdot 3.98E-9$

~ $HA_1 \cdot HA_2 = 10^{2pka} \cdot 1.576E-17$

$\frac{HA_1}{HA_2} = 39.68$

~ $39.68 HA_2^2 = 10^{2pka} \cdot 1.576E-17$

$10^{2pka} = 2.52E18 HA_2^2$ ~ $2pKa = \log(2.52E18 \cdot HA_2^2)$

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What is $\log(ax^2)$?

$$pKa = \log\left(\frac{2.52E18\ H_{A_2}^{2}}{2}\right)$$

for kicks, let $HA_2 = 1E\text{-}5$

$pKa = 4.2$ There is nothing unreasonable about this number @ all.

It seems like you are really on the right track. All you need to know now is HA_2 to peg the acid down.

We have made some progress. It is now easy to formulate in terms of HA_1

$HA_1 = 39.68\ HA_2$ so

$$pKA = \frac{1}{2}\log\left(2.52E18(39.68\ HA_1)^2\right)$$

$$pKa = \frac{1}{2}\log\left(3.97E21\ HA_1^2\right)$$

This says that you have developed things far enough along so that if you know the concentration of the original acid, you know its pKA, or essentially its dissociation level. This seems pretty good.

$pKa = -\log(ka)$ definition $-pKa = \log(ka)$

$2pKa = -\log(ka)$ for us

$-2pKa = \log(ka)$

Now let figure out how you get concentration.
pka means I know ka in terms of concentration also.

lets go back to our ice table.

	HA	H^+	A^-
init	2m	0	0
Δ	$-X$	X	X
eq	$2m-X$	X	X

This means $\frac{X^2}{2m-X} = ka$ but $2m = HA_1$ so

if pka = $-\log(pk)$ then
$pka = -\log\left(\frac{1}{2}\log(3.97E21\,HA_1^2)\right)$

$\frac{X^2}{HA-X} = ka$ or $X^2 - ka(HA-X) = 0$ we know X @ HA_1
$X = 1.58E-4 = c$

but $\cancel{ka} = 2pka = \log(3.97E21\,HA_1^2)$

or

$2C^2 - 2pka(HA-C) = 0 \Rightarrow 2c^2 - \log(3.97E21\,HA_1^2)(HA-c) = 0$
Can you solve

$2c^2 - \log(3.97E21 \cdot HA_1^2)(HA_1 - c) = 0$

or

$2c^2 - \log(3.97E21 \cdot X^2)(X - c) = 0$ where $X = HA_1$
$C = 1.58E-4$

$\boxed{X = 1.58E-4}$ w/ Casio!

so $HA_1 = 1.58E-4$ Molar

This means pka = 7.0 Which is equivalent to water??

This was both a fascinating process and a fascinating result. You might be on the right track but I suspect that something is wrong. But it does seem like there is something to our methods. Let's try again.

Given
HA of Zm concentration
We titrate w/ 0.01M NaOH
Problem What is the Ka of the acid?

Assume we know the initial pH is 3.8.
after 10ml the pH is 4.6

Our initial reaction is $HA \rightleftharpoons H^+ + A^-$

Now, since we can measure pH and if we assume monotomic molar concentrations

$pH = -\log[H^+] = 3.8$ so $H^+ = 10^{-3.8} = 1.58E-4$
So we do know something.
We add 10ml of NaOH 0.01M & the pH change to 4.6

This is $\frac{0.01\text{ moles}}{1000\text{ ml}}(10\text{ ml}) = 1E-4$ moles NaOH
Now, what happens when we add NaOH to a weak acid?

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Jan 01 2016 - A New Year! Collosal Cave, NM (Tucson)

We have been through a blizzard in Three Rivers NM. This has caused quite a disruption in the research progress. Let's see if we can reinstate a problem which culminated our studies in acid-base chemistry.

A great problem, real world application, has been proposed. (via titration)

Problem: Given an initial pH and a Δ in pH (and possibly the equivalence point by titration) can we determine the pKa? (pKa $\rightleftarrows$ Ka)

We started the problem on the previous page. What are the relationships we can use to solve this problem? (5 pages back we started regrouping)

— Sidenote —

A very interesting comment by Timberlake p404 which involves something that I was and am very curious about. He says:

Strontium Hydroxide $Sr(OH)_2$
Calcium Hydroxide $Ca(OH)_2$
and Barium Hydroxide $Ba(OH)_2$

each have LOW solubility, but they dissociate COMPLETELY.

this was exactly one of my questions and still is!

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HH Differential

Now we also know that

$$pH = -\log[H^+]$$

so $H^+ = 10^{-pH}$ so $H^+ = 10^{-4.6}$

$$= 2.51E-5$$

So we do know that $\Delta H^+ = 1.58E-4$

$$- 2.51E-5$$

$$\Delta H^+ = 1.33E-4$$

Corresponding to 1.0E-4 moles NaOH that has been added. The certainly sound interesting.

Lets look @ potential insights from HH:

$pH = pKa - \log\left(\frac{HA}{A^-}\right)$ but

$$\Delta pH = -\frac{1}{2.303\left(\frac{HA}{A}\right)} \Delta\left(\frac{HA}{A^-}\right)$$

Lets look @ ICE & see what else we can learn.
What is the equation involved.

$HA \rightarrow H^+ + A^-$

Now we know something. If the equivalence point has not been reached then all of the NaOH has reacted. This is important. This is equivalent to the 12ml section from before in the titration study. This is not a buffer reaction; it is a titration reaction.

Initial pH ICE table is:

	HA	$\rightleftharpoons$	H^+	$+$	A^-
init	Zm		0		0
Δ	−x		x		x
eq	Zm−x		x		x

but we know H^+ because we measure pH!

so our table is actually:

	HA	$\rightleftharpoons$	H^+	$+$	A^-
init	Zm		0		0
Δ	−1.58E−4		1.58E−4		1.58E−4
eq	Zm − 1.58		1.58E−4		1.58E−4

2

$$\frac{(1.58E-4)^2}{Zm_1 - 1.58E-4} = \cancel{p}Ka$$

Now we also know that

$$\frac{(2.51E-5)^2}{Zm_2 - 2.51E-5} = Ka$$

Dividing the top equation by the bottom we now have:

$$\frac{(1.58E-4)^2}{Zm_1 - 1.58E-4} = \frac{(2.51E-5)^2}{Zm_2 - 2.51E-5}$$

This means

$$(Zm_1 - 1.58E-4)(2.51E-5)^2 = (Zm_2 - 2.51E-5)(1.58E-4)^2$$

$$(Zm_1 - 1.58E-4) = (Zm_2 - 2.51E-5)(39.62)$$

Notice that we also know the ratio of H^+ in each case:

$$\frac{1.58E-4}{2.51E-5} = \underline{\underline{6.29}} \quad = \frac{H_1^+}{H_2^+}$$

This actually does seem therefore a ratio of acid concentration to me.

$$Zm_2 = \frac{Zm_1 - 1.58E-4}{39.62} + 2.51E-5$$

There is also a very interesting relation.

Example: if $Zm_1 = 0.01$
then $Zm_2 = 2.735E-4$

This indicates there is very little acid left.

Eg if $Zm_1 = .001$
then $Zm_2 = 4.635E-5$

$$\frac{x-5}{6} + 2 \overset{?}{=} \frac{x-5}{6} + \cancel{3} \frac{6(2)}{6} = \frac{x-5+12}{6} = \frac{x+7}{6}$$

yes.

therefore:

$$Zm_2 = \frac{Zm_1 - 1.58E-4}{39.62} + 9.94E-4$$

or $Zm_2 = \frac{Zm_1 + 8.36E{-4}}{39.62}$

if $Zm_1 = 1.0M$ then $Zm_2 = .0253\,M$

So the reduction in concentration is

$$\frac{.0253 - 1.0}{1.0} = -97.5\%$$

This is certainly interesting.

When would it be 99.99%?

Let's develop a general relationship:

$H_1^+ = 10^{-pH_1}$

$H_2^+ = 10^{-pH_2}$

Therefore

$$(Zm_1 - H_1^+)(H_2^+)^2 = (Zm_2 - H_2^+)(H_1^+)^2$$

$$Zm_2 = \frac{(Zm_1 - H_1^+)(H_2^+)^2}{(H_1^+)^2} + H_2^+$$

General Relation

or $$Zm_2 = \frac{(Zm_1 - H_1^+)(H_2^+)^2 + (H_1^+)^2(H_2^+)}{(H_1^+)^2}$$

$Zm_1 = 1.0M$

$H_1^+ = 1.58E{-4}$

$H_2^+ = 2.51E{-5}$

Test: $Zm_2 = .025\,M$ Correct!

Example: if $Zm = 1.0$

$H_1^+ = 1.58E{-4}$

$Zm_2 = 1E{-4}$ (= 0.01%)

Then

What is H_2^+

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Setting this up for equation solver, we have

$$(1E-4) - \left[\frac{(1.0 - 1.58E-4)x^2 + (1.58E-4)^2 x}{(1.58E-4)^2}\right] = 0$$

~~This means that~~

~~$1E-4 - [\,..$~~

$x = 1.568E-6$

$pH = -\log[H_2^+] = -\log(1.568E-6) = \underline{\underline{5.80}}$

What about 99.999%

or $1E-5 - [\,\ldots\,] = 0$

$pH = -\log(4.87E-7) = 6.31$

or 99.9999%

or $1E-6$ =

$pH = -\log(1.46E-7) = 6.83$

or $1E-10$

$pH = -\log(9.96E-11) =$

$= = 10.00$

This all gets very interesting. What should happen is that we should be able to determine experimentally the equivalence point from the titration curve .

We can see that pH 7 always when $H^+ = \underline{1E-7}$

This is by definition.

The pt the equilibrium point (only w/ a strong acid, strong base).

We do have a model that give us relative concentration change relative to change in pH. This is certainly interesting. But it is not pka.

We can see that $pka = pH + \log\left(\frac{HA}{A-}\right)$

By our chemical equation if we know ~~A~~ H+ then we know A^- so we would have

$$\cancel{pH_1} = pka = pH_1 + \log\left(\frac{HA}{H_1^+}\right)$$

$$pka = pH_2 + \log\left(\frac{HA}{H_2^+}\right)$$

We need to solve for HA then solve for pka

this is like

$$pka = pH_1 + \log\left(\frac{HA}{C_1}\right)$$

$$pka = pH_2 + \log\left(\frac{HA}{C_2}\right)$$

log

$c\log(x) + d\log(y) = \log(x^c y^d)$

or Subtracting

$$0 = pH_1 - pH_2 + \log\left(\frac{x}{C_1}\right) - \log\left(\frac{x}{C_2}\right)$$

This should be correct.

Can Equation Solver handle this? No solution given.

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This mean

No $\cancel{X}$ $pH_1 + pH_2 = \log\left(\frac{X}{C_1}\right) - \log\left(\frac{X}{C_2}\right)$

or $\log\left(\frac{X}{C_1}\cdot\left(\frac{X}{C_2}\right)^{-1}\right) = 1 - pH_1 + pH_2$

or $\log\left(\frac{X}{C_1}\cdot\frac{C_2}{X}\right) = 1 - pH_1 + pH_2$

or $\frac{C_2 X}{C_1 \cancel{X}} = 10^{1-pH_1+pH_2}$

Is this true?

$\frac{C_2}{C_1} = \frac{2.51E-5}{1.58E-4} = \underline{\underline{0.159}}$

$10^{1-3.8+4.6}$

$= 10^{1.8}$

$\underline{\underline{No}} = 63.10$

No, this is not true.
But it sure is close that

$\frac{1}{.159}(10) \cong 10^{1.8}$

So what is wrong here. The method does seem reasonable.

$\frac{1}{0.159} \cong 10^{0.8}$

The 1.0 term
is in question here

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OK, I found the error. There is no 1 term

So we are back to

$\cancel{-pH_1 + pH_2 + \log}\left(\frac{x}{C_1}\right)$.

$\cancel{pH}_2$

$$pH_1 - pH_2 + \log\left(\frac{x}{C_1}\right) - \log\left(\frac{x}{C_2}\right) = 0$$

$$-0.8 + \log\left(\frac{x}{C_1}\left(\frac{x}{C_2}\right)^{-1}\right) = 0$$

$$\log\left(\frac{x}{C_1} \cdot \frac{C_2}{x}\right) = 0.8$$

for some reason it is $\log\left(\frac{x \cdot C_1}{C_2 \cdot x}\right) = 10^{pH_2 - pH_1}$

$\left[\frac{C_1}{C_2}\right]$ apparently

$$\frac{C_2}{C_1} = 10^{.8}$$

$x = 6.31$ solved fine.

We

$= 6.31$

We definitely have a solution for x under the conditions

$pH_2 - pH_1$

$$\cancel{pH_1 - pH_2} + \log\left(\frac{HA}{H_2^+}\right) - \log\left(\frac{HA}{H_1^+}\right) = 0$$

but why is this reversed?

Also the number solve you seem way too high.

$10^{-.8} = .159$ which make more sense.

It is

$$pH_2 - pH_1 + \log\left(\frac{x}{H_2^+}\right) - \log\left(\frac{x}{H_1^+}\right) = 0$$

You have a sign problem somewhere

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Are we indeed solving for pKa here?

We believe that our expression should be of the form

~~$10^{pH_1 - pH_2} = \log\left(\frac{HA}{C_1}\right)$~~

$10^{-0.8} =$

Your work assumed equal volume

We should have

$$pKa = pH_2 + \log\left(\frac{HA}{H_2^+}\right)$$

$$pKa = pH_1 + \log\left(\frac{HA}{H_1^+}\right)$$

a

$$0 = pH_2 - pH_1 + \log\left(\frac{HA}{H_2^+}\right) - \log\left(\frac{HA}{H_1^+}\right)$$

$pH_2 = 4.6$
$pH_1 = 3.8$
$H_2^+ = 2.51E{-5}$
$H_1^+ = 1.58E{-4}$

$HA = 6.31$
Seems really high to me.

We get a Ka of 3.96E-9 by substitution

$pKa = -\log(3.96E{-9}) = 8.40$

This says that it is a very weak acid that you have selected.

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Can we indeed solve for pka here?

So now change the problem:

Initial pH = 2.1
after 10 ml the pH is 2.8 w/ 0.01 M NaOH
what is the Ka?

this is our relation

$$pH_2 - pH_1 + \log\left(\frac{HA}{H_2^+}\right) - \log\left(\frac{HA}{H_1^+}\right) = 0$$

$H_1^+ = 10^{-2.1} = 7.94E\text{-}3$

$H_2^+ = 10^{-2.8} = 1.58E\text{-}3$

$\boxed{\text{use } HA \cdot \frac{V_a}{V_b}}$ X See ahead

so $HA = x = 7.93E\text{-}3 = .0079\ M$

so $pKa = 2.1 + \log\left(\frac{HA^+}{H_1^+}\right) = 2.1 + \log\left(\frac{7.93E\text{-}3}{7.94E\text{-}3}\right)$

$= 2.099$

So our actual relation is:

$$\Delta pH = \log\left(\frac{HA}{H_1^+}\right) - \log\left(\frac{HA}{H_2^+}\right)$$

$$= \log\left(\frac{HA}{H_1^+} \cdot \frac{H_2^+}{HA}\right) = \log\left(\frac{H_2^+}{H_1^+}\right)$$

how does the conc. of NaOH figure into this?

$$10^{-\Delta pH} = \frac{H_2^+}{H_1^+}$$

This is what you actually have learned here.

$$-\Delta pH = \log\left(\frac{H_2^+}{H_1^+}\right)$$

This ~~does not~~ Still HA has been eliminated.

even better

Take ± or interesting Deviation

$\log\left(\frac{a}{b}\right)$?

This appears to be a truism but not what you needed. You were asked pKa

Latest development

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Let's test the idea on our standard
Chem wiki problem.

Initial $pH_1 = 1.86$
$pH_2 = 3.18$ (added 12.5 ml NaOH 0.3M)

$H_1 = .0138$
$H_2 = 6.61E-4$
$\Delta pH = 1.32$

Assume same molar concentration?

$[HA] =$

note

$$\left[1.32 + \log\left(\frac{HA}{6.61E-4}\right) - \log\left(\frac{HA}{.0138}\right)\right] \cdot \frac{V_a}{V_b}$$

HA = ~~1.93E-3~~? 0.014(2) = 0.28 vs
— 0.3 OK

This is really really interesting
The actual answer is 0.30 So No!
off by 10

Notice 0.14(2) = 0.28 $HA \rightleftharpoons H^+ + A^-$
Remember our assumption of $1M \rightleftharpoons 1M + 1M$

and that $[H^+] = [A^-]$

This says no.

but this is HF which should be equal proportions

Why am I off by a factor of ≅ 2?

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OH, I see the problem. We only added ~~12.5 M~~ 12.5 ml of NaOH to 25 ml. So we are off by a factor of 2. The no of moles added is important relative to the original concentration.

$$\frac{C_a V_a}{C_b} = V_b \quad \frac{C_a}{C_b} = \frac{V_a}{V_b}$$

$$C_a V_a = C_b V_b$$

$$C_a = \frac{C_b \cdot V_b}{V_a}$$ so we needed to divide our answer by the ratio of $\frac{V_b}{V_a} = 0.5$

$$\frac{0.014}{\left(\frac{12.5}{25}\right)} = \underline{\underline{0.28M}}$$

10ml 0.3 NaOH

Let's try the next one

$pH_1 = 1.86 \Rightarrow H_1^+ = .0138$

$pH_2 = 3.00 \quad H_2^+ = 1E{-}3$

$\Delta pH = 1.14$

$$HA = \overset{.014}{\cancel{.0138}} \left(\frac{25ml}{10ml}\right) = .0345$$

We are off by a factor of 10. Why???

Something is still very wrong here.

[redacted]

Jan 02 2015

pKa Determination Project

Because of the problem that occurred, we will change to the Chemwiki problem. There is no need to have hypothetical data.

Therefore our circumstances are::

Ka=6.6E-4 Initial pH is 1.86 using HF 0.3M 25ml
Add 10 ml 0.3 M NaOH pH = 3.00

Truth is, I would like to solve this with an ICE table in addition to HH.
What is our reaction?
His reaction given is $HF + H_2O \rightleftharpoons H^+ + F^-$
This is because he is headed toward using the HH equation. This only requires the acid-base ratio, it does not require any real knowledge other than a portion of the HF is neutralized, and that this changes the acid base ratio. So he is completely avoiding the ICE table approach.
Chemwiki did not really do this with an ice table
$HF + H_2O + NaOH \rightarrow H^+ + A^- + Na^+ + OH^-$
Now we do know that the H^+ neutralize w/ the OH^- to the point of $C_aV_a = C_bV_b$.

Let's try an ICE:

	HF	H_2O	$NaOH$	$\rightleftharpoons H^+$	$+ F^-$	$+ Na^+$	$+ OH^-$
init	7.5E-3	25ml	3E-3	0	0	0	0
Δ	-3E-3	10ml	-3E-3	3E-3 ~~x 3E-3~~	x ~~3E-3~~	3E-3	3E-3
eq	4.5E-3	35ml	0	~~x~~ 3E-3	x ~~x 3E-3~~	3E-3	3E-3

This part is OK.

HF: $25ml\left(\frac{.30 moles}{1000 ml}\right) = 7.5E\text{-}3$ moles

NaOH:

$\frac{0.30 moles}{1000 ml}(10 ml) = 3E\text{-}3$ moles

We know that H^+ & OH^- neutralize up to the point of 7.5E-3 moles

this equation uses actual moles.

We should have $\frac{(3E\text{-}3)(x)}{4.5E\text{-}3} = 6.6E\text{-}4$ ~~.0105~~ (.1286) OK Here

x = ~~.0138~~ ~~3.785E-3~~ .0108

pH = $-\log$(~~3.78E-3~~ .0108) = 2.42

and unfortunately, that is wrong. It is 3.00

Where we went wrong is with the concentration. Now we have 35 ml instead of 25 ml.

Our ~~concentration is now~~ ~~4.5 mole~~

~~$\frac{0.3M}{1000ml}(35ml) = .0105$~~

$\frac{4.5E\text{-}3 moles}{35 ml} = \frac{x\ moles}{1000 ml}$

Concentration of HF

x = .1286 M This is correct

We still have a problem. $\frac{3E\text{-}3 moles}{35 ml}$ ~~(35ml)~~ ~~1000ml~~ $= \frac{x}{1000}$ (H^+) here OK

x = .0857 M H^+ (OK also)

pH =

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Kc=6.6E-4

We are getting closer w/ the ICE table but we still do not have it exactly.

diss.completely

$HF + H_2O + NaOH \rightleftharpoons H^+ + F^- + Na^+ + OH^-$

	HF	H_2O	$NaOH$	H^+	F^-	Na^+	OH^-
init	7.5E-3	25ml	3E-3	0	0	0	0
Δ_1	-x	10ml	-3E-3	x	x	3E-3	3E-3
eq1	7.5E-3-x	35ml	0	x	x	3E-3	3E-3

Now, we know that OH^- reacts w/ ~~[illegible]~~ H^+ to form H_2O

Δ_2	-3E-3	0	0	-3E-3	0	0	-3E-3
eq2	4.5E-3-x	35ml	0	x-3E-3	x	3E-3	0

This should mean that $\frac{(x-3E-3)(x)}{4.5E-3-x} = 6.6E-4$

x = 3.253E-3 this is supposed to be F^-

Supposedly HH can be used now:

Now HH is actually: $pH = pKa + \log\left[\frac{A^-}{HA}\right]$

$$= -\log(6.6E-4) + \log\left(\frac{3.25E-3}{1.247E-3}\right) = 3.6$$ NOT QUITE

Lets work out concentrations

A^- $\frac{3.253E-3\text{mol}}{35\text{ml}} = \frac{x}{1000\text{ml}}$ x=.093M

HF $\frac{1.247E-3\text{mol}}{35\text{ml}} = \frac{x}{1000}$ x=

This is how a partial titration
is solved.

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Now, the actual answer is that H^+ is 3E-3 moles.
and that HF is 4.5E-3 moles.

We also learn that HH requires molar concentrations,
not actual moles. Look this up.

Now, why the above?
Apparently because it reacts completely w/ the HF
but how do you know this?
Because the moles of NaOH added are less than
the original concentration of HF. This is why.
It reacts completely.

Therefore the actual ICE table is:

$HF + H_2O + NaOH \rightarrow H^+ + F^- + Na^+ + OH^- + H_2O$

	HF	H_2O	$NaOH$	⇌ H^+	+ F^-	+ Na^+	+ OH^-	H_2O
init	7.5E-3mol	25ml	3E-3Mol	0	0	0	0	25ml
Δ	-3E-3mol	10ml	-3E-3mol	3E-3	3E-3	3E-3	3E-3	10ml
eq	4.5E-3mol	35ml	0 mol	3E-3mol	3E-3mol	3E-3mol	3E-3mol	

Since there is no "X", there is no reason to use an
equilibrium expression. HH is the preferred route.
I would however like to be able to go that route.
B4 mistake

$pH = pKa + \log\left[\frac{A^-}{HA}\right]$ but these must be molar concentrations!

$A^- = \frac{3E\text{-}3 \text{ moles}}{35ml} = \frac{X}{1000}$ $X = .0857 \underline{\underline{M}}$

$HA = \frac{4.5E\text{-}3}{35ml} = \frac{X}{1000}$ $X = .1286 \underline{\underline{M}}$

$pH = -\log(6.6E\text{-}4) + \log\left[\frac{.0857}{.1286}\right] = 3.00$ Excellent

$3 = \log(x)$

$10^3 = x$

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Now we know one of our major mistakes. HH uses molar concentration, not the actual moles. We may now be in a better position to frame our problem.
Let's use the Chemistry Problem as a template

Initial pH 1.86 (HF 0.3M 25ml)
$pH_2 = 3.00$ (10 ml NaOH, also 0.3M)
~~ka~~

molar concentration

HH: $pH_2 = pK + \log\left[\frac{A^-}{HA}\right]$ (Notice we may have had an error here)
this means
$pH_2 - pH_1 = \log\left(\frac{A^-}{HA}\right)_2 - \log\left(\frac{A^-}{HA}\right)_1$

You assumed HA is a constant. This is not true!
$1.14 = \log\left(\frac{A_2^-}{HA_2}\right)_2 - \log\left(\frac{A_1^-}{HA_1}\right)_1$

Now we know $c\log(x) + d\log(y) = \log(x^c y^d)$ so

$1.14 = \log\left(\frac{A_2^-}{HA_2} \cdot \frac{HA_1}{A_1^-}\right)$ and this is quite different from before

This mean

molar concentration

$$\frac{A_2^- \; HA_1}{HA_2 \; A_1^-} = 13.80$$

Let's start to learn what we can about this ratio.

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With the initial pH we have

$HF \rightleftarrows H^+ + A^-$

$HF \quad H^+ + A^-$

Since the pH initial = 1.86 we know that $pH = -\log(H^+)$

so $H^+ = 10^{-pH} = 10^{-1.86} = .0138$ ~~moles not molar concentration~~ molar concentration, not # moles

we also know (in this case, that we started out with ~~7.5 moles~~ 7.5E-3 mole HF

$\frac{7.5E\text{-}3 \text{ moles}}{25 ml} = \frac{X}{1000} \quad X = 0.3M \; HF = HA_1$

for H^+ we have

~~$\frac{.0138 \text{ moles}}{25 ml} = \frac{X}{1000}$~~ ~~$X = .552M \; H^+$~~

~~which also means we have~~ $.552M \; A^-$,

this means that we have $\frac{A_2^-}{HA_2} \cdot \frac{(\cancel{.552M} \; 0.3M)}{(\cancel{.552M} \; .014M)} = 13.80$

or $\frac{A_2^-}{HA_2} = \frac{\cancel{25.397}}{.644}$ and this is true.

So we are on the right track here.

The equation is therefore valid:

$$\Delta pH = \log\left(\frac{A_2^-}{HA_2} \cdot \frac{HA_1}{A_1^-}\right)$$

$$\boxed{\text{or } \frac{A_2^-}{HA_2} \cdot \frac{HA_1}{A_1^-} = 10^{+\Delta pH}}$$

This is a valid relationship.

$HA \rightleftharpoons H^+ + A^-$

Given that:

$$\frac{A_2^-}{HA_2} \cdot \frac{HA_1}{A_1^-} = 10^{\Delta pH}$$

We can now start to investigate ICE relationships

Let's go back to our original problem.

$pH_1 = \cancel{3.8}\ 2.5$ 50 ml of unknown HA

$pH_2 = 4.6$ adding 10 ml of 0.001 NaOH

If we assume equal molar ratios formed we may write (since $H^+ = A^-$)

$$\frac{H_2^+}{HA_2} \cdot \frac{HA_1}{H_1^+} = 10^{\Delta pH}$$

$pH = -\log(H^+)$

molar concentration

for H_2^+ we have $H_2^+ = 10^{-pH} = 2.512E-5$ M

H_1^+ " " $H_1^+ = 10^{-\cancel{3.8}\ 2.5} = \cancel{1.585E-4}$ M

Therefore, we already know that we have 3.162E-3

$$\frac{HA_1}{HA_2}\left(\frac{2.512E-5}{\cancel{1.585E-4}\ 3.162E-3}\right) = 10^{\cancel{1.2}\ 2.1} \quad \text{or}$$

or $\frac{HA_1}{HA_2} = \frac{\cancel{100.00}}{15846.8}$ That was really very interesting. The numbers seem to be a [illegible]

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Now, if we have a relationship that

$C_aV_a = C_bV_b$

then we have $\frac{C_a}{C_b} = \frac{V_b}{V_a}$

or $C_a = \frac{C_b \cdot V_b}{V_a}$

Does this hold for weak acid strong base titrations?

No, it does not!.

This only holds for acids & bases that completely dissociate.

So at this point, we know the ratio, but not the actual concentration.

	HA	$+ H_2O$	$+ NaOH$	$\rightarrow H^+$	$+ A^-$	$+ Na^+$	$+ OH^-$	$+ H_2O$
Init	X moles	50ml	1.E-5	0	0	0	0	50ml
A_1	-1E-5 moles	10ml	-1E-5	1E-5	1E-5	1E-5	1E-5	10ml
A_2	X-1E-5 moles	60ml	0	1E-5	1E-5	1E-5	1E-5	

H^+: ~~1.585E-4~~ 3.162E-3 moles / 1000ml = X / 50ml   X = ~~7.925E-6~~ 1.581E-4 moles

NaOH $\frac{.001 \text{ moles}}{1000 \text{ ml}}$ (10ml) = ~~1E-4 moles~~ 1E-5 moles

molar conc!

so we know that $\frac{HA_1}{HA_2} = 15846.8$ and that

~~$pH = pKa + \log\left[\frac{A^-}{HA}\right]$~~ we know in this case that

~~$A^- = \frac{1E-5 \text{ moles}}{60 \text{ ml}} = \frac{X}{1000}$~~ ~~X = 1.67E-4M~~ for

This may not be necessary.

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It seems to me that we know

$HA_1 = X$ moles

$HA_2 = X - 1E\text{-}5$ moles

$\frac{HA_1}{HA_2} = 15846.8$

and HA_1's molar concentration is $\frac{X}{50 ml} = \frac{X_{1m}}{1000 ml}$

or $X_{1m} \cdot 50 = 1000 \cdot x$
$X_{1m} = 20X$

and for HA_2 $\frac{X - 1E\text{-}5}{60 ml} = \frac{X_{2m}}{1000}$

$X_{2m} = \frac{(X - 1E\text{-}5)(1000 ml)}{60 ml}$

or $X_{2m} = (X - 1E\text{-}5) \cdot 16.67$

So $\frac{HA_1 (\text{Molar Conc})}{HA_2 (\text{Molar Conc})} = \frac{20 \cdot x}{(X - 1E\text{-}5)(16.67)} = \frac{1.20X}{(X - 1E\text{-}5)}$

We therefore have a relationship that says

$\frac{1.20X}{(X - 1E\text{-}5)} = 15846.8$

or $X =$ ~~1.000E-5~~
1.0001E-5

Problem on this Page - Why?
Using pH for H+ you are not getting the
$HF \rightarrow H^+ + F^-$ same result as on
the next page. Why?

They say that HA_2 is ~~[illegible]~~. 1E-9M.
Does that make any sense to you.
It is interesting that I have a solution but
How do I have any idea if it is right?
No it does not make any sense w/a

Okay, it looks like back to Chemwiki.
We have a model that make sense.

$$\frac{A_2^-}{HA_2}\,\frac{HA_1}{A_1^-} = 10^{\Delta pH}$$

$pH = -\log[H^+]$
$+\log[H^+] = -pH$
$[H^+] = 10^{-pH}$

Chemwiki
$pH_1 = 1.86 \Rightarrow H_1^+ = ..0138$ in ~~25ml~~ 1000ml
$pH_2 = 3.00 \Rightarrow H_2^+ = 1E-3$ in ~~35ml~~ 1000ml

Definition of pH: $pH = -\log[H^+]$ defined in molar concentration

$$\frac{.0138\text{ moles}}{1000\text{ ml}} = \frac{X}{25\text{ ml}} \qquad X = 3.45E\text{-}4 \text{ moles in } 25\text{ ml}$$

You are exactly correct; from Chemwiki $H^+ = 0.014M$
And you must be correct by definition of H_2^+

Therefore we know that

$$\frac{1E\text{-}3M}{HA_2}\cdot\frac{HA_1}{0.0138\,M} = 10^{1.14} \text{ or}$$

$$\frac{HA_1}{HA_2} = 190.49$$

We have $HA_1 = .286M$
We have $HA_2 = .1286M$

The Ice Method / Succeeds

This is a check on our derived formula using the Chem wiki Template and it shows that it works perfectly.

$$\frac{A_2^-}{HA_2} \cdot \frac{HA_1}{A_1^-} = 10^{\Delta pH}$$

$$\frac{A_2^-}{HA_2} \cdot \frac{HA_1}{A_1^-} = 10^{(3.0-1.86)} = 13.80$$

We started out with

$$\frac{7.5E-3 \text{ moles HF}}{25 \text{ ml}} = \frac{X}{1000 \text{ ml}} \quad X = \boxed{0.3M\ HF} \text{ or } HA_1$$

this is actually 0.286 after dissociation

So

$$\frac{A_2^-}{HA_2} \cdot \frac{0.3M}{A_1^-} = 13.80$$

We ended with

$$\frac{4.5E-3 \text{ moles HF}}{35 \text{ ml}} = \frac{X}{1000 \text{ ml}}$$

HA_2 $\boxed{X = 0.1286M}$

So

$$\frac{A_2^- \ (0.3M)}{(0.1286M)\ A_1^-} = 13.80$$

$$\text{So } \frac{A_2^-}{A_1^-} = 5.92$$

and

$A_1 = \boxed{.014M}$ so

$$\frac{A_2^-}{.014M} = 5.92 \text{ or } \boxed{A_2^- = 0.083M} \checkmark$$

and since we have

$$\frac{3E-3 \text{ moles}}{35 \text{ ml}} = \frac{X}{1000 \text{ ml}} \quad X = 0.086M \checkmark$$

The Use of pH method - Fails

Trying to find out why we have a problem.

We determine $H_1^+ = A_1^- = 0.014\ M$ Correct ✓

A_2^- is not matching. Why? but we have

This fails $H_2^+ = 10^{-3} = 1E{-}3\ M$ by pH NOT

This works $H_2^+ (= A_2^-) = 0.083\ M$ by ICE - why? OK

We have $HA_1 = 0.3\ M$ OK

Problem is Here

We have $HA_2 = 0.1286\ M$ OK

Notice HH equation is not molar Concentration! It is moles! Actually it can be either, the ratio stays the same. This is a huge difference.

in moles $HA_1 = 7.5E{-}3$

in moles $HA_2 = 4.5E{-}3$

but for our equation these values must be in molar concentration.

It also seems our A_1^- & A_2^- must be in molar concentrations.

This is the problem

$\frac{1E{-}3\ \text{moles}}{35\ \text{ml}} = \frac{X}{1000\ \text{ml}}$ $X =$ for some reason it should be 3E-3 moles?

for HH, you can use either

$$pH = pKa + \log\left(\frac{A^-}{HA}\right) \text{ or } pH = pKa - \log\left(\frac{HA}{A}\right)$$

I prefer this one.

So we have the problem that has emerged.

In one solution, by the ICE table we have H_2^+ = 3E-3 moles
notice this is in 35 ml
so $\frac{3E-3 \text{ mole}}{35 \text{ ml}} = \frac{x}{1000}$ x = .0857 Molar

Now, in a direct measurement, we have the pH as = 3.0 @ the end of the partial titration. This implies the H_2^+ Concentration is

10^{-3} = .001 M
So how can this possibly be.
Lets make sure that we are in the same units.

I really do not understand the problem.
I should be able to get the same result from 2 different methods.

We can see that we have a problem. The problem is that a developed method succeeds that is based upon the use of ICE data, but it fails with the use of pH data. Both data sets represent the same problem.

Three out of four critical data points match up. The one that does not is H_2+.

Here is an interesting proposition. What if we take ΔpH based on H^+ concentration instead of ICE.
One has to wonder if there just is a problem with the pH determination? What if my ideas about dissociation were correct?
Let's see how much difference there is:
$pH = -\log[H^+]$ // which is a molar definition.

by ICE: $pH = -\log[.083M] = 1.08$
by pH: $pH = -\log[1E-3] = 3.0$

and this is exactly the nature of the problem. They do not coincide. And this leads me to believe there may be a problem w/ the ICE method.
What if we used 0.083 instead of 1E3 (1.08 pH vs 3.0)?
Remember the original pH starts at 1.86
So it is impossible that H^+ after 10 ml of titration w/ NaOH decreases the pH from 1.86 to 1.08.
Here lies the problem. Let's find it.
Remember they used HH to solve their problem, they never used ICE in a complete sense, only a partial sense. There is a problem here.

Since we know we agree w/ essentially 4 out of 5 data points we can solve in reverse for H_2^+.

$$H_2^+ = A_2^- = \frac{10^{\Delta pH} \cdot HA_2 \cdot A_1^-}{HA_1} = \frac{10^{(30-1.86)}(0.12\underline{86}M)(0.014M)}{0.3M} = \underline{\underline{0.083M}}$$

This number therefore, would seem to be in error as it needs to be 1E-3 by definition alone.
The no. most likely to be incorrect, therefore is HA_2.

$\frac{A_2^-}{HA_2} \frac{HA_1}{A_1^-} = 10^{\Delta pH}$ Page 195

Then as recently I had my doubts about several times along the way. I am seriously beginning to have my doubts about HF_2.

Think about the quantities here
ΔpH is fixed in our problem and our relationships.
$1.86 - 3.0$

A_1 fixed by straight dissociation and Ka
A_2 fixed by the pH value.
HA_1 fixed @ 0.3M, actually 0.286 of un dissociated
HA_2 this seems to be potentially in error.

Lets solve for HA_2 and see what it should be.

$$HA_2 = \frac{A_2^-}{10^{\Delta pH}} \cdot \frac{HA_1}{A_1^-} = \frac{(1E-3M)}{10^{(3-1.86)}} \cdot \frac{0.286M}{.014M}$$

$= 1.48E-3$ and this sounds a lot more reasonable to me than 0.1286
$\frac{.1286}{.286}$ would only decrease the acid content by 45%
This does not sound likely to me.
Lets revisit my ICE?

$HF + H_2O + NaOH \Leftrightarrow H^+ + F^- + Na^+ + OH^- - H_2O$

	HF	~~H_2O~~	~~NaOH~~	H^+	F^-	Na^+	OH^-	H_2O
Init	0.286M	~~25ml~~	~~3E-3~~	~~.014~~	.014	0	0	25ml
Δ	-3E-3	~~10ml~~	-3E-3	-3E-3	-3E-3	3E-3	3E-3	10ml
	.286 - 3E-3							

Page 196

It seems to me that the H_2^+ Concentration is therefore

~~$.014 - 3E{-3} = .011$~~

~~$pH = -\log(.011) = 1.96$~~

No, what we need are the Moles, not the molar Concentrations

	HF	H_2O	NaOH	H^+	F^-	Na^+	OH^-	H_2O
init	7.15E-3 mol	25 ml	3E-3 mol	3.5E-4	3.5E-4	0	0	25 ml
Δ	-3E-3	10 ml	-3E-3	+3E-3	+3E-3	3E-3	3E-3	10 ml
eq	4.15E-3	35 ml	0	3.35E-3	3.35E-3			

HF_1: $.286M \Rightarrow \dfrac{.286M}{1000ml} = \dfrac{x}{25ml}$ $\quad x = 7.15E{-3}$ moles

H^+: $.014M = \dfrac{.014 \text{ moles}}{1000ml} = \dfrac{x}{25ml}$ $\quad x = 3.5E{-4}$ moles

HF_2: $\dfrac{4.15E{-3} \text{ moles}}{35ml} = \dfrac{x}{1000ml}$ $\quad x = 0.119M$

$H_2^+ = A_2^- = \dfrac{3.35E{-3} \text{ moles}}{35ml} = \dfrac{x}{1000}$ $\quad x = .096M$

This leads to $\overset{\text{this is wrong.}}{\dfrac{.096M}{.119M}} \cdot \left(\dfrac{.286M}{.014M}\right) \overset{?}{=} 10^{(3-1.86)}$

Close!!! $\quad 16.48 \overset{?}{=} 13.80$

This is now reasonable and original work!

Page 197

There may (and appear) to be some nuance left in the numbers and interpretations, but the numbers have finally set in and they are reasonably stable. The ICE approach, with original work, seems to have cleared things up quite a bit.

The mystery remains to me, why if something has a pH of 3.0, why isn't the H^+ concentration @ that time 1E-3?
How can it be .096M as I have solved for?
This part is still not clear to me.

But here ~~is a heck of~~ a question.
How can ~~we start out w/~~ a weak acid that dissociates to a certain H^+ content (ie .014M), then add a strong base, and have an H^+ content that is now higher? (.096M) This makes no sense.

Not the case

yes the case

pH : -log (.014) = 1.86
pH : -log (.096) = 1.02 This is impossible!

Let's go to the Chemlab Simulator

0.3M HF does indeed give a pH of 1.86 good.
It lists: F^- 3.44E-4 moles
HF in solution: 7.156E-3 moles
H^+ 3.44E-4 moles
H_2O 1.388 moles (25 gms)

Chemlab Completely agrees with this

Indeed, when 10 ml of 0.3M NaOH is added, the pH is 3.01

Can not get any closer than that.
Chemwiki is spot on.
Composition is:

F^-	3.03E-3 moles
HF	4.47E-3 moles
H^+	3.4E-5 moles
OH^-	0.00 moles
Na^+	3.00E-3 moles
H_2O	1.946 moles (35 gms)

ChemLab is all in moles

H^+ for original solution:

$$\frac{3.44E-4 \text{ moles}}{25 \text{ ml}} = \frac{x}{1000 \text{ ml}} \qquad x = .01376M \qquad pH = 1.86$$

$$H^+ \quad \frac{3.4E-5}{35 \text{ ml}} = \frac{x}{1000} \qquad x = \underline{9.71E-4}M \qquad pH = 3.01$$

notice

Start w/ HF $\overset{H_2O}{\rightleftharpoons}$ H^+ + F^- + H_2O

	HF	H^+	F^-	H_2O
init	~~7.5E-3 moles~~ .13	0	0	25ml
Δ	-x	x	x	
eq	.3 ~~7.5E-3~~ -x	x	x	

$$\frac{.0138 \text{ moles}}{1000 \text{ ml}} = \frac{x}{25}$$

$$n \; \frac{x^2}{\cancel{7.5E-3-x} \; .13-x} = 6.6E-4 \qquad x = .0138M$$

$x = 3.45E-4$ moles

This discovery alone is very important

A lesson here: Equilibrium expressions must be in molar concentration form!!!

OK, we now have a model in ChemLab with Dissociation.

Partial Titration (10 ml)
First Real Success
Tied in with Chemlab Coaching.

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This is a valuable very [illegible] & insightful ice table

Now lets create a 10 ml NaOH Ice table and match it up with ChemLab. Then we will be in business.

	HF	H_2O	NaOH	H^+	F^-	Na^+	OH^-	H_2O
Init	7.5E-3 mo	25 ml	3E-3 mo	0	0	3E-3	3E-3	25 ml
Δ	-3E-3	10 ml	-3E-3	3⊗	3E-3	0	-3E-3	10 ml
eq	4.5E-3	35 ml	0	3.5E-5 ⊗ moles (calc) from HH	3E-3	3E-3	0	35 ml

everything here is in moles.

see 3 pages ahead to be right. OK! I solved it ↑ This table IS GOOD ↑

HF, after dissociation is
0.3M − .0138M = .286M

$\frac{.286M}{1000 ml} = \frac{X}{25 ml}$ X = 7.15E-3 moles

NaOH: $\frac{0.3 moles}{1000 ml}$ (10 ml) = 3E-3 moles

$NaOH + HF + H_2O \rightarrow Na^+ + OH^- + H^+ + F^- + H_2O$
7.15E-3

HF: 3.45E-4 − 3E-3 + 7.15E-3 = 4.5E-3

How to get H^+

$pH = pka + \log\left(\frac{A^-}{HA}\right)$

3.18
pH = 3.18 + (−.176) = 3.0

HF_2: $\frac{4.5E-3 moles}{35 ml} = \frac{X}{1000}$
X = .1286M

HF_1: $\frac{7.5E-3}{25 ml} = \frac{X}{1000}$

X = 0.3M

Partial Titration
First Real Success
Tried w/ ChemLab Coaching

And now that we have pH
We can solve for H^+

$pH = -\log(H^+)$

$\log H^+ = -pH$

$H^+ = 10^{-pH}$ so $H^+ = 10^{-3.0} = .001M = 1E-3M$

$\frac{1E-3M}{1000ml} = \frac{x}{35ml}$ $x = 3.5E-5$ mols

Ok, we now know how H^+ is computed within a partial titration. You use HH to get the pH and then go back at H^+.

Now we try:
$\frac{A_2^-}{HA_2} \frac{HA_1}{A_1^-} = 10^{\Delta pH}$ Nope, it has a problem.

this was WRONG! $A_2^- \neq H_2^+$!!!

$\frac{\overset{.0857}{\cancel{1E-3M}}}{.1286M} \cdot \frac{0.3M}{.0138M} = 10^{3-1.86}$

ok now.

$= \cancel{.409}$??? Close- $14.49 = 13.80$

This says that your developed relationship does not work.

1. My relationship has an error in it
2. Chem Lab has an error.

This is what caused so much difficulty for me.

~~Check this.~~ Check Molar Concentration vs Moles.

Chemistr PDF is in WPS, not [illegible]

Page 183

We are getting closer w/ the ICE table but we still do not have it exactly.

Ka=6.6E-4

	HF	+ H_2O	+ NaOH diss.completely	⇌	H^+	+ F^-	+ Na^+	+ OH^-	+ H_2O
Init	7.5E-3	25ml	3E-3		0	0	0	0	
Δ_1	-x	10ml	-3E-3		x	x	3E-3	3E-3	
eq1	7.5E-3-x	35ml	0		x	x	3E-3	3E-3	

Now, we know that OH^- reacts w/ H^+ to form H_2O

Δ_2	-3E-3	0	0	-3E-3	0	0	-3E-3	
eq2	4.5E-3-x	35ml	0	x+3E-3	x	3E-3	0	

This should mean that $\frac{(x-3E-3)(x)}{(4.5E-3)-x} = 6.6E-4$

$x = 3.253E-3$ (x) this is supposed to be F^-

Supposedly HH can be used now:

Now HH is actually: $pH = pka + \log\left[\frac{A^-}{HA}\right]$

$= -\log(6.6E-4) + \log\left(\frac{3.25E-3}{1.247E-3}\right) = 3.6$ NOT QUITE

Lets work out Concentrations

A^- $\frac{3.253E-3mol}{35ml} = \frac{x}{1000ml}$ $x = .093M$

HF $\frac{1.247E-3mol}{35ml} = \frac{x}{1000}$ $x =$

This is how a partial titration
is solved.

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Now, the actual answer is that H^+ is 3E-3 moles.
and that HF is 4.5E-3 moles.

We also learn that HH requires molar concentrations,
not actual moles. Look this up.

Now, why the above?
Apparently because it reacts completely w/ the HF
but how do you know this?
Because the moles of NaOH added are less than
the original concentration of HF. This is why.
It reacts completely.

Therefore the actual ICE table is:

$HF + H_2O + NaOH \rightleftharpoons H^+ + F^- + Na^+ + OH^- + H_2O$

	HF	H_2O	NaOH	$\rightleftharpoons H^+$	$+ F^-$	$+ Na^+$	$+ OH^-$	H_2O
init	7.5E-3mol	25ml	3E-3Mol	0	0	0	0	25ml
Δ	-3E-3mol	10ml	-3E-3mol	3E-3	3E-3	3E-3	3E-3	10ml
eq	4.5E-3mol	35ml	0 mol	3E-3mol	3E-3mol	3E-3mol	3E-3mol	

Since there is no "x", there is no reason to use an
equilibrium expression. HH is the preferred route.
I would however like to be able to go that route.
B4 mistake

$$pH = pKa + \log\left[\frac{A^-}{HA}\right]$$ but these must be molar concentrations!

$$A^- = \frac{3E\text{-}3 \text{ moles}}{35 ml} = \frac{x}{1000} \quad x = .0857 \underline{\underline{M}}$$

$$HA = \frac{4.5E\text{-}3}{35ml} = \frac{x}{1000} \quad x = .1286 \underline{\underline{M}}$$

$$pH = -\log(6.6E\text{-}4) + \log\left[\frac{.0857}{.1286}\right] = 3.00$$

Excellent

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Now, if we have a relationship that

$C_aV_a = C_bV_b$

then we have $\frac{C_a}{C_b} = \frac{V_b}{V_a}$

Does this hold for weak acid strong base titrations?

or $C_a = \frac{C_b \cdot V_b}{V_a}$

No, it does not!.

This only holds for acids & bases that completely dissociate.

So at this point, we know the ratio, but not the actual concentration.

$HA + H_2O + NaOH \rightarrow H^+ + A^- + Na^+ + OH^- + H_2O$

	HA	H_2O	$NaOH$	H^+	A^-	Na^+	OH^-	H_2O
Init	x moles	50ml	1.E-5	0	0	0	0	50ml
A_1	-1E-5 moles	10ml	-1E-5	1E-5	1E-5	1E-5	1E-5	10ml
A_2	x-1E-5 moles	60ml	∅	1E-5	1E-5	1E-5	1E-5	

H^+: $\frac{\cancel{1.585E-4}\ 3.162E-3 \text{ moles}}{1000\text{ml}} = \frac{x}{50\text{ml}}$ $x = \cancel{7.925E-6}\ 1.581E-4$ moles

NaOH $\frac{.001 \text{ moles}}{1000 \text{ ml}}(10\text{ml}) =$ ~~1E-4 moles~~ 1E-5 moles

molar conc!

so we know that $\frac{HA_1}{HA_2} = 15846.8$ and that

~~$pH = pKa + \log\left[\frac{A^-}{HA}\right]$ we know in this case that~~

~~$A^- = \frac{1E-5 \text{ moles}}{60 \text{ ml}} = \frac{x}{1000}$ $x = 1.67E-4$ M for~~

This may not be necessary.

Page 195

$$\frac{A_2^-}{HA_2}\,\frac{HA_1}{A_1^-} = 10^{\Delta pH}$$

Then as smoothly as I lost my doubts about several times along the way, I am seriously beginning to lose my doubts about HF_2.

Think about the quantities here

ΔpH is fixed in our problem and our relationships.

1.86 − 3.0

A_1 fixed by straight dissociation and Ka

A_2 fixed by the pH value.

HA_1 fixed @ 0.3M, actually 0.286 after dissociation

HA_2 this seems to be potentially in error.

Lets solve for HA_2 and see what it should be:

$$HA_2 = \frac{A_2^-}{10^{\Delta pH}} \cdot \frac{HA_1}{A_1^-} = \frac{1E{-}3M}{10^{(3-1.86)}} \cdot \frac{0.286M}{.014M}$$

$= 1.48E{-}3$ and this sounds a lot more reasonable to me than 0.1286

$\frac{.1286}{.286}$ would only decrease the acid content by 45%

This does not sound likely to me.

Lets revisit my ICE:

$HF + H_2O + NaOH \Leftrightarrow H^+ + F^- + Na^+ + OH^- + H_2O$

	HF	H_2O	NaOH	H^+	F^-	Na^+	OH^-	H_2O
Init	0.286M	25ml	3E-3	.014	.014	0	0	25ml
Δ	.286-3E-3	10ml	-3E-3	-3E-3	-3E-3	3E-3	3E-3	10ml
eq	.286-3E-3							

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It seem to me that the H_2^+ concentration is therefore

~~$.014 - 3E{-}3 = .011$~~

~~$pH = -\log(.011) = 1.96$~~

No, what we need are the moles, not the molar concentrations

	HF	H_2O	NaOH	H^+	F^-	Na^+	OH^-	H_2O
init	7.15E-3 mol	25 ml	3E-3 mol	3.5E-4	3.5E-4	0	0	25 ml
Δ	-3E-3	10 ml	-3E-3	+3E-3	+3E-3	3E-3	3E-3	10 ml
eq	4.15E-3	35 ml	0	3.35E-3	3.35E-3			

$$HF_1: .286M \Rightarrow \frac{.286M}{1000ml} = \frac{x}{25ml} \qquad x = 7.15E{-}3 \text{ moles}$$

$$H^+: .014M = \frac{.014 \text{ moles}}{1000ml} = \frac{x}{25ml} \qquad x = 3.5E{-}4 \text{ moles}$$

$$HF_2: \frac{4.15E{-}3 \text{ moles}}{35ml} = \frac{x}{1000ml} \qquad x = 0.119M$$

$$H_2^+ = A_2^- = \frac{3.35E{-}3 \text{ moles}}{35ml} = \frac{x}{1000} \qquad x = .096M$$

this is wrong.

This leads to $\frac{.096M}{.119M} \cdot \left(\frac{.286M}{.014M}\right) \overset{?}{=} 10^{(3-1.86)}$

Close!!! $16.48 \overset{?}{=} 13.80$

This is now reasonable and original work!

Partial Titration (10 ml)

First Real Success

Tied in with Chemlab Coaching.

Page 199

This is a workable very insightful table

Now lets create a 10 ml NaOH Ice table and match it up with Chemlab.
Then we will be in business.

everything here is in moles.

	HF	H_2O	NaOH	H^+	F^-	Na^+	OH^-	H_2O
init	7.5E-3 mol	25 ml	3E-3 mol	0	0	3E-3	3E-3	25 ml
Δ	-3E-3	10 ml	-3E-3	3 ⓧ	3E-3	0	-3E-3	10 ml
eq	4.5E-3	35 ml	Ø	3.5E-5 moles (calc) ⓧ	3E-3	3E-3	Ø	35 ml

see 3 pages ahead later right.

from HH OK!

I solved it ↑ This table is GOOD ↑

HF, after dissociation is
Ø.3M - .0138M = .286M

$\frac{.286M}{1000 ml} = \frac{x}{25 ml}$ x = 7.15E-3 moles

NaOH: $\frac{Ø.3 moles}{1000 ml}$ (10 ml) = 3E-3 moles

NaOH + HF + H_2O → Na^+ + OH^- + H^+ + F + H_2O

7.15E-3

HF: 3.45E-4 - 3E-3 + 7.15E-3 = 4.5E-3

How to get H^+

HF_2: $\frac{4.5E-3 \text{ moles}}{35 ml} = \frac{x}{1000}$

x = .1286M

pH = pka + log $\left(\frac{A^-}{HA}\right)$

HF_1: $\frac{7.5E-3}{25 ml} = \frac{x}{1000}$

3.18

pH = 3.18 + (-.176) = 3.0

x = Ø.3M

So the actual Concentration of H_2^+ is .001M with a pH of 3.

$pH = -\log[.001] = 3$

but Chemwiki has:

$\frac{3E-3 \text{ moles}}{35 ml} = \frac{X}{1000}$ $X = .0857M$

So Chemwiki is correct.
The ~~pro~~ ~~pro~~ problem is that the assumption that $A_2^- = H+$ IS WRONG.

$A_2^- = F^- = 3E-3$ moles $\neq .0857M$

But:

$\frac{3.5E-5}{35ml} = \frac{X}{1000ml}$

$X = .001M$

$H+ = 3.5E-5 \cong .001 \underline{\underline{M}}$

$pH = -\log[H^+]$

$H^+ = 10^{-pH}$

So they are not the same at all.
HH actually requires $\frac{A^-}{HA}$

not $\frac{H^+}{HA}$

The lesson: They are NOT the same thing!

Now, fix my derivation and we will be in business

$\frac{3.5E-5}{35 ml} = \frac{X}{100 ml}$ $X =$

I solved for H_2^+ !!

The interesting thing is that without HH we could not have figured out H_2^+.

And similarly, without HH, Chemwiki could not have figured out the pH.

So even the ICE table came up deficient here. Now lets go to our derivation.

The problem w/ your derivation is that you assumed the same thing, that $A_2^- = H_2^+$. THIS IS WRONG! YOU CANNOT DO THIS.

1. Ok - I have found my problem.
2. I have verified Chemwiki.
3. I have used the simulator to great advantage
4. I have learned that $A_2^- \neq H_2^+$.

We are now getting set up again to work with a completely unknown acid, ie acidic protein.

Solving for H_2^+

Notice transformation to molar concentrations.

$$\frac{X(\cancel{3E\text{-}3\text{ moles}})\ 1.05E\text{-}4M}{\cancel{4.5E\text{-}3\text{ moles}}\ 1.575E\text{-}4M} = 6.6E\text{-}4$$

$\frac{3E\text{-}3\text{ moles}}{1000\text{ ml}}$ $\frac{X}{35\text{ ml}}$ X= 1.05E-4

$\frac{4.5E\text{-}3}{1000\text{ ml}}$ $\frac{X}{35\text{ ml}}$ X= 1.575E-4

QED.

X= 9.9E-4 = H_2^+
pH = -log(9.9E-4)
= 3.00
Great

Solved H_2^+ without HH, used ICE

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A method to identify the pka of an unknown acid

Jan 03 2016 Colossal Cave Tucson NM

I have solved for H_2^+ using a full ICE table!

Very good, no HH was needed.
It is a single variable as X.

Now that the Chemlab simulator has guided us through our problem, we can revisit the problem of working to identify a complete unknown!
We also have an intriguing relationship that we have derived.

Our tools of solution include:
1. The ever revealing ICE table (reaction table)
2. My developed relationship involving ratios
3. Direct pH measurements
4. Titration-volume-molarity data
5. A differential relationship exists also.

Let's go to work on it.
Given
1. 50 ml of a completely unknown acid.
2. measured pH is 3.8
3. Titrate w/ 10 ml of 0.01 NaOH
4. measured pH after is 4.6

Question: What is the pka of the unknown acid?

Relations

$$\frac{A_2^- \, HA_1}{HA_2 \, A_1^-} = 10^{\Delta pH}$$

$$\frac{d(\log x)}{dx} = \frac{1}{x \cdot \ln(10)} = \frac{1}{2.303x}$$

$$pH = pKa + \log\left(\frac{A^-}{HA}\right)$$

~~Dec~~ Jan 03 2016 Collosal Cave, Tucson NM

$$dpH = \frac{1}{2.303\left(\frac{A^-}{HA}\right)} d\left(\frac{A^-}{HA}\right)$$

First, we know H_1^+ & H_2^+ direct from msmt:

$pH = -\log[H^+] \Rightarrow H^+ = 10^{-pH}$

$H_1^+ = 10^{-3.8} = 1.585E-4$ M

$H_2^+ = 10^{-4.6} = 2.512E-5$ M (Mole-Concentrations!)

This is already very useful information.

From our derived relationship:

$$\frac{A_2^- \, HA_1}{HA_2 \, A_1^-} = 10^{\Delta pH}$$

Now, what we have learned is that H^+ does not necessarily equate to A^-. This was a critical failure. It was the same prior to titration, however.

So we do know, however, already that:

$$\frac{A_2^- \, HA_1}{HA_2 \, A_1^-} = 10^{(4.6-3.8)} = 6.310$$

Now, it does seem as though A_1^- is very likely to $= H_1^+$. It does assume that equimolar dissociation take place.

* If this is the case, then

$$\frac{A_2^- \, HA_1}{HA_2} = (6.310)(1.585E-4) = 1.000E-3$$

or

$$\frac{A_2^- \, HA_1}{HA_2} = 1.000E-3$$

Now it seems as though we need to involve titration.

A Method to Identify

Page 205

Carrying forward, we have

$$\frac{A_2^- HA_1}{HA_2}^{*} = 1.000E-3$$

The original unknown acid (assuming monoprotic) has a dissociation..

$$HA \rightleftharpoons H^+ + A^-$$

and .IN MOLAR CONCENTRATION ONLY!!

$$\frac{[H_1^+][A_1^-]}{HA_1} = Ka$$

and the only thing we know here is $[H^+]$
But if we assume $H_1^+ = A_1^-$ before titration
then we have

$$\frac{(1.585E-4M)^2}{HA_1} = ka \qquad \text{or } Ka = \frac{(1.585-4)^2}{HA_1}$$

or

$$Ka = \frac{2.512E-8}{HA_1}$$

this is certain to be a useful relationship.

It says if we know HA_1 we know Ka.
That is good.

This is what we learn from the original dissociation. Now let's go to titration.

the pka of an Unknown Acid.

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$HA + H_2O + NaOH \rightleftarrows H^+ + A^- + Na^+ + OH^- + H_2O$

An ICE table:

	HA	H_2O	NaOH	H^+	A^-	Na^+	OH^-	H_2O
Init (M!)	HA_1	50ml	0	1.6E-4M	1.6E-4M	0	0	50ml
Init (m)	HA_1	50ml	0	8E-6m	8E-6m	0	0	50 ml
Δ_1	0	10ml	1E-4m	0	0	0	0	10ml
eq_1	0	60ml	1E-4m	8E-6	8E-6	0	0	60ml
Δ_2	0	0	-1E-4	0	0	1E-4	1E-4	0
eq_2	HA_1	60ml	0	8E-6	8E-6	1E-4	1E-4	60ml

H^+ moles: $\frac{1.6E-4 \text{ moles}}{1000 \text{ ml}} = \frac{x}{50 \text{ ml}}$ x= 8E-6 moles

NaOH moles: $\frac{.01 \text{ moles}}{1000 \text{ ml}} = \frac{x}{10 \text{ ml}}$ x = 1E-4

NaOH ~~m~~ ~~60~~ ml: $\frac{1E-4 \text{ moles}}{10 \text{ ml}} = \frac{x}{60 \text{ ml}}$ x=6E-4

H^+_1 ~~m~~ ~~60~~ ml: $\frac{8E-6 \text{ moles}}{50 \text{ ml}} = \frac{}{60 \text{ ml}}$

Not true, the moles Stay the same. Only molarity Changes.

Δ_3	HA_1-1E-4	0	0	X	1E-4	0	-1E-4	0
eq_3	HA_1-1E-4	60ml	0	8E-6+X	8E-6+1E-4	1E-4	0	60ml

[illegible] = HA_1 - 1E-4 moles

HA_2 (M): $\frac{HA_1 - 1E\text{-}4 \text{ moles}}{60 \text{ ml}} = \frac{X}{1000 \text{ ml}}$ x(60) = $(HA_1 - 1E\text{-}4) \cdot 1000$

So $HA_2(M) = \frac{(HA_1 - 1E\text{-}4)}{16.67} M$ x = $\frac{(HA_1 - 1E\text{-}4)}{16.67} M$

~~8E-6~~

Equilibrium expressions require Molarity!

$H_2^+ = (8E-6 + X)$ moles

We actually know H_2^+ directly from measurement.

$H_2^+ = 2.512E-5M$

We also should know A_2^-

A_2^- moles = 8E-6 moles

this is wrong! A_2 moles = 8E-6 + 1E-4!

This was wrong! recalculate!

so

$$\frac{8E-6 \text{ moles}}{60ml} = \frac{x}{1000ml} \qquad x = 1.333E-4\ M$$

Therefore we should be able to develop an expression.

$$\frac{(1.333E-4M) - HA_1}{\frac{(HA_1 - 1E-4)M}{16.67}} = 1.000E-3$$

$$\left[\frac{(1.333E-4M) - HA_1}{1}\right] \cdot \frac{16.67}{(HA_1 - 1E-4)M} = 1.000E-3$$

or $$\frac{16.67\left[(1.333-4M) - HA_1\right]}{(HA_1 - 1E-4)M} = 1.000E-3$$

This is like

$$\frac{C_1(C_2 - x)}{(x - C_3)} = C_4$$

A Method to Identify the pka of a Completely unknown acid.

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or

$C_1(C_2-x) = C_4(x-C_3)$ or $C_1(C_2-x)-C_4(x-C_3)=0$

$C_1 = 16.67$
$C_2 = 1.333E-4$
$C_3 = 1E-4$
$C_4 = 1.000E-3$

$X = 1.333E-4\,(M)$

Supposedly $X = HA$, !!!

and Supposedly $Ka = \frac{2.512E-8}{1.333E-4} = 1.884E-4$

and $pKa = -\log(Ka) = -\log(1.888E-4) = \underline{\underline{3.72}}$

This goes a long way in identifying an weak acid.

What is the relationship between pka & Ka?
It is the pH @ which the acid is in equilibrium.

This would place the acid as similar to that of formic acid (pka = 3.72)

Theoretically you can now determine the pka of an unknown acid. This a great accomplishment.

[redacted]

Jan 03 2016 (Continued)

The method to potentially identify the pKa of a completely unknown acid is very rewarding. It has taken a great deal of work to accomplish this. I am now in a position to test this upon a simulated example, since a Chemwiki HF template or even using Chemlab.

Kevin Ahern in Oregon is very tuned into the significance of this. He even had a podcast. This would be helpful to hear.

It is now a good time to regroup now.

[redacted]

Jan 05 2016 Colossal Cave NM

We are in a place to examine how the simulator works and if we can apply it to our problem.

We can use HF but assume we know nothing about it.
1. Use 50 ml of 0.3M HF get pH 1.86
2 add 10 ml of 0.01 NaOH get pH 1.93

Can you estimate pKa for this acid?
How does it compare to actual?

$H_1^+ = 10^{-1.86} = .0138M$
$H_2^+ = 10^{-1.93} = .0117M$

$\frac{A_2^- HA_1}{HA_2 A_1^-} = 10^{(1.93-1.86)} = 1.1749$ a ratio
Before Titration!
If we assume that $A_1^- = H_1^+$ (vise verse) then

$\frac{A_2^- HA_1}{HA_2} = 1.1749(\underset{\text{Molarity}}{.0138M}) = .0162$ Molarity.

and $\frac{[.0138M]^2}{HA_{1\,\text{molarity}}} = Ka$ or $Ka = \frac{1.904E-4}{HA_{1\,\text{molarity}}}$

Now we have two relations calculated.
Now we go to titration & an ICE table.

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$HA + H_2O + NaOH \rightleftarrows H^+ + A^- + Na^+ + OH^- + H_2O$

	HA	H_2O	NaOH	H^+	A^-	Na^+	OH^-	H_2O
pH, meas init,	HA_1	50ml	0	.0138M	.0138M	0	0	50ml
Convert to moles Init 2	HA_1 mols	50ml	0	6.9E-4m	6.9E-4m	0	0	50ml
add NaOH Δ_1	HA_1 mols	10ml	.01M	6.9E-4m	6.9E-4m	0	0	10ml
Convert NaOH to moles Δ_2	HA_1 mols	0	1E-4m	6.9E-4m	6.9E-4m	0	0	0
Reset volume eq1	HA_1 mols	60ml	-1E-4m	6.9E-4m	6.9E-4m	1E-4	1E-4	60ml
Dissoc into NaOH Δ_3	1E-4moles	0	0	$\boxed{X}$	1E-4	0	-1E-4	0
HA_2 eq2	$(HA_1 - 1E-4$	60ml	0	X+6.9E-4	6.9E-4+1E-4	1E-4	0	60ml

Equilibrium expression require conversion to molarity.
Two relationship carry forward.

$$\frac{\overset{molarity}{A_2^-}\ \overset{molarity}{HA_1}}{HA_2} = .0162 \text{ molarity} \qquad Ka = \frac{1.904E-4}{HA_1 \text{ molarity}}$$

molarity or

$$\frac{(HA_1 - 1E-4) \text{ moles}}{60 \cdot \cancel{1000} \text{ ml}} = \frac{X}{\cancel{60\text{ml}}\ 1000}$$

2 moles or

$$(HA_1 - 1E-4)\overset{1000}{\cancel{60}} = X \cdot \overset{60}{\cancel{1000}}$$

$$HA_2 = \underset{molarity}{} \quad X = \frac{(HA_1 - 1E-4)}{\cancel{1000}\ 60}\overset{1000}{\cancel{60}} = \overset{moles}{(HA_1 - 1E-4)}\overset{16.67}{\cancel{0.6}} = HA_2 \overset{Molarity!}{} \quad \underline{\text{Molarity}}$$

HA₂ molarity

$$\frac{\overset{molarity}{A_2^-}(HA_1)^{\text{molarity}}_{\text{moles}}}{\overset{16.67}{\cancel{0.6}}\underset{moles}{(}\underset{moles}{HA_1 - 1E-4})} = .0162 \text{ Molarity}$$

~~Assumed to be Molarity~~!

this entire expression converts to molarity

We know A_2^-:

$A_2^- = 6.9E-4 + 1E-4 = 7.9E-4$ <u>moles</u> not molarity!

Therefore $\cancel{\frac{1.317E-3 / HA_1}{HA_1 - 1E-4}} = \cancel{.0162}$

x

H^+: $\frac{.0138 \text{ moles}}{1000 \text{ ml}}$ = ~~x 30ml~~ / ~~50ml~~ 50ml = x = 6.9E-4 moles

NaOH: $\frac{.01 \text{ moles}}{1000 \text{ ml}}$ (10ml) = 1E-4 moles

---

so

~~1.31E-3 · HA − .0162(HA₁ − 1E-4) = 0~~

~~or think like~~

~~1.317E-3x − .0162(x − 1E-4) = 0~~

~~x = 1.088E-5~~

Not true. Need Molarity for A_2^-

We have some problem w/ mole vs molarity.

A_2^- = $\frac{7.9E\text{-}4 \text{ moles}}{60 \text{ ~~1000~~ ml}}$ = $\frac{x}{1000 \text{ ~~60~~ml}}$ x = ~~4.14E-5M~~ 0.013 M molarity!

Now, we also have a term of HA₁ that involved moles vs molarity issues

We should be OK now.

but to use HA₁ in the numerator as a molarity to solve for x

we will have to express it in terms of moles to be consistent w/ the denominator

Think about this. In the denominator x will be moles

in the numerator x will be Molarity. They cannot be one

number ~~so you must convert the~~ Lets let HA = Moles for now.

So we have molarity / moles molarity.

.013 ~~4.14E-5~~ · HA₁ (molarity) / 16.67 ~~0.6~~(HA₁ − 1E-4) (moles, moles) = .0162 or .013 ~~7.9E-5~~ x − .0162 (x − 1E-4) = 0
*16.67!

x = 1.0506 ~~1.005~~E-4 moles HA₁

so $\frac{1.0506 \text{ ~~1.005~~E-4 moles}}{60 \text{ ml}} = \frac{x}{1000}$

x = HA₁ = 1.75 ~~1.675~~E-3 Molarity

molarity = ~~.001675~~ .00175

vs actual 0.3M

So we have a problem

I wonder why I am ~~off~~ by a factor of 171, why?

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So you are way off, by a factor of 171.
Why?
Could it be that the small pH change introduces a lot of error?
Lets try 0.1M NaOH instead 10ml

Initial pH 1.86
10ml after ~~1ml~~ of 1.0. M NaOH ph = 3.48 much better
Is HF a weak acid? It is weak.

$H_1^+ = 10^{-1.86} = .0138M$
$H_2^+ = 10^{-3.48} = 3.31E-4$ $\quad 10^{\Delta pH} = 41.69$

$\frac{A_2^- HA_1}{HA_2 A_1^-} = 41.69$

Assume $A_1^- = H_1^+ = .0138$

So

$\frac{A_2^- HA_1}{HA_2} = 3021.01$ $\qquad \frac{[.0138M]^2}{HA_1} = Ka$

$Ka = \frac{1.904E-4}{HA_1}$

Ice table

	HA	H_2O	NaOH	H^+	A^-	Na^+	OH^-	H_2O
init	HA_{1m}	50ml	0	.0138M	.0138M	0	0	50
Conv H form Δ_1	0.	0	0	6.9E-4m	6.9E-4m	0	0	0
add NaOH Δ_2	0	10ml	.01m	0	0	0	0	10ml
Diss NaOH Δ_2	0	0	-.01m		.01m	+.01m	+.01m	0
Neutralize HF Δ_3	-.01m	0	0		0	0	-.01	0
eq.	HA_1-.01m	60ml	0	X	.01+6.9E-4m	.01m	0	60ml

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NaOH

$\frac{1.00\text{ moles}}{1000\text{ ml}}\ 10\text{ ml} = .01\text{ mole}$

$H^+ : \frac{.0138\text{ moles}}{1000\text{ ml}} = \frac{X}{50\text{ ml}}$ $X = 6.9E{-4}\text{ moles}$

$\overset{**}{H_2^+} :$ ~~$\frac{(X+.01)\text{ mole}}{1000\text{ ml}} = \frac{X\text{ mols}}{60\text{ ml}}$~~ $X \doteq 60_{ml}\frac{(X+.01)\text{ mols}}{1000\text{ ml}} =$

$H_2^+ = \frac{X+.01\text{ moles}}{60\text{ ml}} = \frac{y}{1000\text{ ml}}$ $y = \overset{ml}{1000}\frac{(X+.01\text{ moles})}{60\text{ ml}} = 16.67(X+.01)$ Molarity

so $H_2^+ = 16.67(X+.01m)$ (Molarity)

Molarity

So here is what we should know

$16.67(X+.01\text{ moles}) = 3.31E{-4}$ Molarity

[Molarity]

$X = .167M$

.3 $\frac{.01\text{ moles}}{60\text{ ml}} = \frac{X}{1000}$

$X =$

There are some problem of some kind. Let's review the ICE structure from our template.

The ICE table uses all moles.

Equilibrium expressions use molarity.

The expressions I developed both use molarity.

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This ICE table works/

Using the most engineered Chemlab solution:

It looks like I do have it.

	HA	H_2O	NaOH	H^+	A^-	Na^+	OH^-	H_2O
Init	HA_1 (m)	50ml	.01m	0	0	.01	.01	50ml
Δ	-.01m	10ml	-.01m	X	.01m	0	-.01	10ml
eq	HA_1(m) - .01m	60ml	0	X	.01m	.01	0	60ml

Converted to Molarity

$$\frac{HA_2(m)(.01m)}{HA_1(m) - .01} = Ka$$

and that

but we also know that

$$\frac{A_2^- \, HA_1}{HA_2 \, A_1^-} = 10^{\Delta pH}$$ molarity.

$$Ka = \frac{[H^+][A^-]}{HA}$$

Need Molarity

Therefore $Ka = \frac{[X][.01m]}{HA_1(m) - .01m}$ converted to. in terms of molarity.

~~a Ka = H_2~~

We know some things:

A_2^- 60ml $\frac{.01 \text{moles}}{\cancel{1000ml}} = \frac{X}{\cancel{60ml}\ 1000}$ $X = 0.167M$

So

$$\frac{0.167M \cdot HA_1(M)}{HA_2(M) \cdot A_1^-} = 10^{\Delta pH}$$

$$\frac{HA1(\text{moles})}{50\text{ ml}} = \frac{X(M)}{1000}$$ $(M)X(50ml) = HA1(m) \cdot 1000$

$$X_M = \frac{HA1(m) \cdot 1000}{50}$$

So $HA_1(M) = HA1(m) \cdot 20$

It looks like I do have it.

HA: 50 ml of unknown concentration, call it HA_1 (moles)

NaOH .. $\frac{1.0 \text{ moles}}{1000 \text{ ml}} (10 \text{ ml}) = .01$ moles

Therefore now we know that:

$$\frac{0.167(M) \cdot HA_{1(m)} \cdot 20}{(HA_{1(m)} - .01m)_M \cdot A_1^-} = 10^{\Delta pH}$$

but we know that $A_1^- = H_1^+ = 0.0138M$

So now we have

$$\frac{3.34 \cdot HA_{1(m)}}{(HA_{1(m)} - .01m)_M (.0138M)} = 10^{\Delta pH}$$

or $$\frac{242.029 \cdot HA_{1(m)}}{(HA_{1(m)} - .01m)_M} = 10^{\Delta pH}$$

now $\frac{HA_{1(m)} - .01m}{60 \text{ ml}} = \frac{X}{1000}$ $\quad X(60) = 1000(HA_{1(m)} - .01(m))$

or $X = 16.67(HA_{1(m)} - .01m)$

and X here actually equals HA_2 (M)

so

$$\frac{242.029 \cdot HA_{1(m)}}{16.67(HA_{1(m)} - .01m)} = 41.69$$

$HA_{1(m)} = .015m$ $\quad \frac{.015 \text{ moles}}{60 \text{ ml}} = \frac{X}{1000}$

calculated

$X = 0.25M$

HF known vs 0.3M

We may have it!

147.36 AR

It does look like we have it.
What is the error in the function?

What are the steps of the method?

1 Measure initial pH
2. Measure final pH after partial titration
3 Construct an ICE table
4. Use my relationship, going after one term @ a time:

$$\frac{A_2^- \cdot HA_1}{HA_2 \cdot A_1^-} = 10^{\Delta pH}$$

4a. We know $A_1^- = H_1^+$ which $= 10^{-pH_1}$

4b. A_2^- we know from titration, convert to molarity

4c. Next we convert HA_1 to a molarity term.

4d. Next we convert HA_2 to a molarity term also, but it remains in terms of HA_1

5. We know $10^{\Delta pH}$

6. We solve for $HA_{1(m)}$ using Casio

7. We convert $HA_{1(m)}$ to HA_1 (M) and that is our answer for the original concentration.

[redacted] [redacted]

B - We should now be able to solve for ka

$$g: k_a = \frac{(.0138M)^2}{0.25M} = 7.62E-4$$

and $pK_a = -\log(k_a) = -\log(7.62E-4)$

$= 3.12$ which is what we get for HF

and the actual value is: vs $\underline{\underline{3.14}}$

This is <u>superb</u>.

Therefore quality pH measurements are paramount to the success of the project.

It is time now to relax and enjoy the fruits of my work by starting to investigate a new lab!

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Pop (people per sq mi)	Air Traffic
0<100	0 None
1<1000	1 Light
2<10,000	2 Med
3<100,000	3 Heavy
4>100,000	4 Blitz

Mem Date Location State Weather
Time Pop Vis Traffic PM T°C Wind Dir %RH Elev Vis

01-10-16 Cllosal Cave Tucson ~~NM~~ Az Mostly Cldy
0945 0 None 2 9° 1-SW 41% 3700 50

* * * Note: Jan 11 2016 Tucson local news reports unusual pristine air
conditions due to El Nino conditions & heavier rain than normal

31 01-11-16 Tucson (Colossal Cave) NM Clear Az
1330 0 None - 2 21°C 3-NW 15% 3700 70

01-12-16 Tucson (Laundry) outside of Speedway Blvd ~~NM~~ Az - Clear
1230 3 None 20 23°C 1-SE 7% 2500 70

33 01-13-16 Casa Grande (Sam's Parking Lot) Az Clear
1915 3 None 5 16°C 2-NW 30% ~~2500~~ 1500 650

01-14-16 Travel from Casa Grande to Sonoran Natl Mon.

01-15-16 Sonoran Natl Mon, AZ Mostly Cldy, Aerosol Trails E-W
1030 0 Light 2 16°C 5-SE 30° 1000 70
Note: E-W Aerosol Trails Confined to Interstate Corridor

01-16-16 Sonoran Natl Mon, Az Medium Aerosol Operations in Clear Sky
Medium Aerosol Activity along I-8 corridor & heavy operations to
south. Visibility to south affected; approx 40 miles (& east)
Visibility in immediate area and remaining quadrants
not significantly affected, eg 70 mi.
0915 0 Medium 2 16°C 1-E 34% 1000 40-70+

Aerosol* Operation Photos Taken

Also Non Outdoor Next Page

PM 2.5 #3

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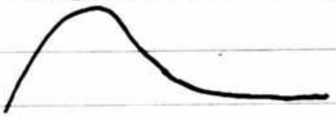
Aerosol operation photos Taken 01-16-16 Sonoran Natl Mon. - Med. Aerosol operations in Clear Sky
1115 0 Medium 20 24°C 2-E 19% 1000' 40
Increasing occlusion @ ground level over surrounding sky and quadrants. A typical aerosol operation is in progress. Air quality meter shows this change in a perfectly representative fashion. This is the first data point collection that shows the presence and impact of a definitive aerosol operation.

"Cirrus Blanket" into majority.
01-16-16 Sonoran Natl Mon. - Med. Aerosol Operations Completed
1500 0 Light 11 25°C 2-E 15% 1000' 50
Visibility now slightly increased to south ~ 80 mi. and East
Visibility to west & north ~ 40 mi. decreased.
Mostly ~~Largely~~ occluded sky ~~Hasty~~.

39 01-16-16 Sonoran Natl Mon: - Altocumulus 90% Cloud Cover
1930 0 None 3 13°C 0-NA 13% 1000' 60
Night observation.
This require you exponential harmonic regression
Also Try D Plot.



01-17-17 Sonoran Natl Mon - Clear
0930 0 None 2 18°C 2-SE 29% 1000' 60
Haze to N (Phoenix area) & S-SE (Tucson area)
Clear in vicinity, to W & NW. Return of sky conditions of relative normality

01-18-17 Sonoran Natl Mon - Strato diffuse cumulus ~~Stratus~~, Cloudy
1000 0 None(Visible) 2 18°C 2-SE 28% 1000' 60

* 01-19-17 Sonoran Nat Mon - Mostly Sunny ~~Clear~~, "High Clouds", Significant Aerosol Operation to SE (Tucson area), Diffuse Layer of Aerosols Overhead
Aerosol Operation Photos Taken 0915 0 Heavy to S-SE 2 20°C 2-SE 23% 1000' 60-70 to W 40 to S.
E- Pri Heavy flight path Tucson, Med Overhead 60-70 to E 40 to N

A method to identify the pka of an unknown acid

Jan 03 2016 Colossal Cave Tucson NM

I have solved for H_2^+ using a full ICE table!

Very good, no HH was needed.
It is a single variable as X.

Now that the Chemlab simulator has guided us through our problem, we can revisit the problem of working to identify a complete unknown!
We also have an intriguing relationship that we have derived.

Our tools of solution include:
1. The ever revealing ICE table (reaction table)
2. My developed relationship involving ratios
3. Direct pH measurements
4. Titration-volume-molarity data
5. A differential relationship exists also.

Let's go to work on it.

Given
1. 50 ml of a completely unknown acid.
2. Measured pH is 3.8
3. Titrate w/ 10 ml of 0.01 NaOH
4. Measured pH after is 4.6

Question: What is the pka of the unknown acid?

the pka of an unknown Acid.

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$HA + H_2O + NaOH \rightleftarrows H^+ + A^- + Na^+ + OH^- + H_2O$

An ICE table:

	HA	H_2O	$NaOH$	H^+	A^-	Na^+	OH^-	H_2O
init(M!)	HA_1	50ml	0	1.6E-4M	1.6E-4M	0	0	50ml
init(m!)	HA_1	50ml	0	8E-6m	8E-6m	0	0	50 ml
Δ_1	0	10ml	1E-4m	0	0	0	0	10ml
eq_1	0	60 ml	1E-4m	8E-6	8E-6	0	0	60ml
Δ_2	0	0	-1E-4	0	0	1E-4	1E-4	0
eq_2	HA_1	60ml	0	8E-6	8E-6	1E-4	1E-4	60ml

H^+ moles: $\frac{1.6E-4 \text{ moles}}{1000 \text{ ml}} = \frac{x}{50 \text{ ml}}$ $x = 8E-6$ moles

NaOH moles: $\frac{.01 \text{ moles}}{1000 \text{ ml}} = \frac{x}{10 \text{ ml}}$ $x = 1E-4$

NaOH ~~in~~ 60 ml: $\frac{1E-4 \text{ moles}}{10 \text{ ml}} = \frac{x}{60 \text{ ml}}$ $x = 6E-4$

H^+_1 ~~in~~ 60ml: $\frac{8E-6 \text{ moles}}{50 \text{ ml}} = \frac{}{60 \text{ ml}}$

Not true, the moles stay the same. Only molarity changes.

Δ_3	HA_1-1E-4	0	0	X	1E-4	0	-1E-4	0
eq_3	HA_1-1E-4	60ml	0	8E-6+X	8E-6+1E-4	1E-4	0	60ml

HA_2 moles = HA_1 - 1E-4 moles

HA_2 M: $\frac{HA_1 - 1E-4 \text{ moles}}{60 \text{ ml}} = \frac{X}{1000 \text{ ml}}$ $X(60) = (HA_1 - 1E-4) \cdot 1000$

$$\text{So } HA_2(M) = \left(\frac{HA_1 - 1E-4}{16.67}\right) M \qquad X = \left(\frac{HA_1 - 1E-4}{16.67}\right) M$$

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$HA + H_2O + NaOH \Leftrightarrow H^+ + A^- + Na^+ + OH^- + H_2O$

	HA	H_2O	$NaOH$	H^+	A^-	Na^+	OH^-	H_2O
pH, measurement 1	HA_1	50ml	Ø	.0138M	.0138M	Ø	Ø	50ml
Convert to moles Init 2	HA_1 moles	50ml	Ø	6.9E-4m	6.9E-4m	Ø	Ø	50ml
add NaOH Δ_1	HA_1 moles	10ml	.01M	6.9E-4m	6.9E-4m	Ø	Ø	10ml
Convert NaOH to moles Δ_2	HA_1 moles	Ø	1E-4m	6.9E-4m	6.9E-4m	Ø	Ø	Ø
Merge volume eq_1	HA_1 moles	60ml	-1E-4m	6.9E-4m	6.9E-4m	1E-4	1E-4	60ml
Dissociate NaOH Δ_3	1E-4 moles	Ø	Ø	$\boxed{X}$	1E-4	0	-1E-4	Ø
HA_2 eq_2	HA_1-1E-4	60ml	Ø	X+6.9E-4	6.9E-4+1E-4	1E-4	Ø	60ml

Equilibrium expressions require conversion to molarity.
Two relationships carry forward:

$$\frac{\overset{\text{molarity}}{A_2^-}\ \overset{\text{molarity}}{HA_1}}{\underset{\text{molarity}}{HA_2}} = .0162\ \text{molarity} \qquad Ka = \frac{1.904E-4}{HA_1\ \text{molarity}}$$

or

$$\frac{(HA_1 - 1E-4)\text{moles}}{60 \cdot \cancel{1000}\text{ml}} = \frac{X}{\cancel{60}\text{ml}\ 1000}$$

2 moles of

$$(HA_1 - 1E-4)\overset{1000}{\cancel{60}} = X \cdot \overset{60}{\cancel{1000}}$$

HA₂ = molarity

$$\overset{n}{X} = \frac{(HA_1 - 1E-4)}{\cancel{1000}\ 60}\overset{1000}{\cancel{60}} = \overset{\text{moles}}{(HA_1 - 1E-4)}\overset{16.67}{\cancel{0.6}} = HA_2 \quad \text{Molarity!} \quad \underline{\underline{\text{Molarity}}}$$

$$\frac{\overset{\text{molarity}}{A_2^-}(HA_1)^{\text{molarity moles}}}{\overset{16.67}{\cancel{0.6}}(\underset{\text{moles}}{HA_1} - \underset{\text{moles}}{1E-4})} = .0162\ \text{Molarity}$$

this entire expression converts to molarity

~~This needs to be Molarity!~~

We know A_2^-:

$A_2^- = 6.9E-4 + 1E-4 = 7.9E-4$ moles not molarity!

Therefore $\xcancel{\frac{1.31E-3/HA_1}{HA_1 - 1E-4}} = .0162$

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So we are way off, by a factor of 171.

Why?

Could it be that the small pH change introduce a lot of error?

Lets try 0.1M NaOH instead ~10ml

Initial pH 1.86

10ml after ~~10ml~~ of 1.0. M NaOH ph = 3.48 much better

Is HF a weak acid? It is weak

$H_1^+ = 10^{-1.86} = .0138M$ ΔpH ≈

$H_2^+ = 10^{-3.48} = 3.31E-4$ $10^{\Delta pH} = 41.69$

$$\frac{A_2^- HA_1}{HA_2 A_1^-} = 41.69$$

Assume $A_1^- = H_1^+ = .0138$

So

$$\frac{A_2^- HA_1}{HA_2} = 3021.01$$

$$\frac{[.0138M]^2}{HA_1} = Ka$$

≈

$$Ka \approx \frac{1.904E-4}{HA_1}$$

Ice table

	HA	H_2O	NaOH	H^+	A^-	Na^+	OH^-	H_2O
init	HA_{1m}	50ml	0	.0138M	.0138M	0	0	50
conv H+ to moles Δ1	0	0	0	6.9E-4m	6.9E-4m	0	0	0
add NaOH Δ2	0	10ml	.01m	0	0	0	0	10ml
Diss NaOH Δ2	0	0	-.01m		.01m	+.01m	+.01m	0
Neutalize HF Δ3	-.01m	0	0		0	0	-.01	0
eq	$HA_1 - .01_m$	60ml	0	x	.01+6.9E-4m	.01m	0	60ml

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This ICE table works

Using the ~~host~~ engineered Chemlab solution:

It looks like I do have it.

	HA	H_2O	NaOH	H^+	A^-	Na^+	OH^-	H_2O
Init	$HA_{1(m)}$	50ml	.01m	0	0	.01	.01	50ml
Δ	−.01m	10ml	−.01m	X	.01m	0	−.01	10ml
eq	$HA_{1(m)}-.01m$	60ml	0	X	.01m	.01	0	60ml

Converted to Molarity

$$\frac{HA_{2(m)}(.01)m}{HA_{1}(m)-.01} = Ka$$

and that

but we also know that

$$\frac{A_2^- \, HA_1}{HA_2 \, A_1^-} = 10^{\Delta pH} \quad \text{molarity.} \qquad Ka = \frac{[H^+][A^-]}{HA}$$

Need Molarity

Therefore $Ka = \frac{[X][.01m]}{HA_1(m)-.01m}$ converted to in terms of molarity.

~~$Ka = H_2^+$~~

We know some things:

A_2^- 60ml

$$\frac{.01\text{moles}}{\cancel{1000ml}} = \frac{X}{\cancel{60ml}\;1000} \qquad X = 0.167M$$

So

$$\frac{0.167M \cdot HA_1(M)}{HA_2(M) \cdot A_1^-} = 10^{\Delta pH}$$

$$\frac{HA1(\text{moles})}{50\,ml} = \frac{X}{1000}(M) \qquad (M)\,X(50ml) = HA1_{(m)} \cdot 1000$$

$$X_M = \frac{HA1_{(m)} \cdot 1000}{50}$$

So $HA_1(M) = HA1_{(m)} \cdot 20$

Non Outdoor PM2.5

Mem		Date	Tim	Locatn	Pop	PM	T°	%RH
27	✓	01-08-16	1030	Cracker Barrel Rest Tucson AZ	3	2	23°	31%
30	✓	01-10-16	1000	RV Reading Terry, Tucson AZ	0	15	20°	45%
32		01-12-16	1230	Laundromat Tucson, AZ	3	10	22°C	19%
~~33~~ 34		01-14-16	1000	Cracker Barrel Rest Casa Grande AZ	2	8	18°C	30%
		01-28-16	1145	Cracker Barrel Rest Tucson AZ	3	25	25C	13%
		02-11-16	1615	Cochise Stronghold - Campground - Distant Campfire	0	80	19°C	18%
		02-12-16	1515	Apache Fly Ash Plant 8 miles N. of Pearce	1	45	32°C	2%
		02-12-16	1500	Hwy191, Shoulder N of Pearce AZ 3 Consecutive, Deisel Semi's w/Dust kicked up	1	≥500	32°C	2%

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Jan 11 2015 - A Bonding Lab

	Melting	Ethanol	Water	Conductivity
Calcium Chloride	>2min ④	insoluble	soluble	② 166.1 ms
Citric Acid	19.5sec ②	soluble	soluble	④ 0.0 ms
Phenyl Salicylate	8 sec ①	soluble	insoluble	④ 0.0 ms
Pot. Iodide	>2min ④	insoluble	soluble	③ 118.9 ms
Sodium Chloride	>2min ④	insoluble	soluble	① 269.0 ms
Sucrose	24sec ③	soluble	soluble	④ 0.0 ms

Now we get to start thinking about the Character of these compounds, eg ionic or Covalent.

NaCl is apparently not a molecule. It does not exist alone. Likely the same for $CaCl_2$

Identification of Unknowns

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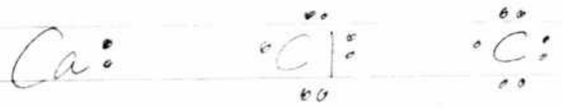
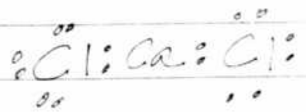
Calcium Chloride $CaCl_2$



Now, ionic means the electrons transfer, not share.



What is the geometry? How would I know?
Why does it have a high melting point?
Why is it soluble in H_2O
Why is it insoluble in alcohol?
Is it crystalline?

Time to learn about ionic substances.

Zumdahl says exactly what we are up to. Melting point, solubility (in our case, ethanol and H_2O) and conductivity. So let's see how we use it.
These msmts are taken to "determine the fundamental nature of materials".

Ok, 1st topic is conductivity. High conductivity msmts mean high ionic content. That means ionic bonds. So already we see that KI, NaCl, & $CaCl_2$ are almost certain to be ionic materials w/ ionic bonds. Ionic bonds also have high melting points. Same thing happened here under the Bunsen burner. So you already have separated these salts out. That they all dissolve in water must also be important; study solubility more further.

Page 225 ~~Identification of Unknowns~~

Date Location State Weather
~~Citric Acid $C_6H_8O_7$~~

Time PM Time Pop Vis Traffic PM T° Wind Dr %RH Elev Vis

So:

0915 2 01-19-17 (Cont)
1100 8 Targets of operation appear to be Phoenix & Tucson.
1245 15 Considerable occlusions to ~~the~~ NE & SE over the
1415 40 metro areas. Local area in S.N.M. remains reasonably
1445 45 Clear w.r.t. visibility.
1515 52
1525 57 01-19-17 Sonoran Natl Mon. - Mostly Sunny
1630 36 Heavy Haze Over Phoenix & NE Mild haze to S-SE
1730 5 1100 0 ~~None~~ Light 8 24°C 1-SE 16% 1000' 40 N&S 60 E&W
1800 2 Hwy 84 & I-8 Junction

~~1245 0~~ nearest town is

* * 01-19-17 ~~Hw~~ Stanfield AZ "High Clouds" "Cirrus Blanket"
1245 0 Light 15 26°C 4-NE 16% 1000' 20-S
Aerosol Bank to Immediate South 40-E,N
50-W

Aerosol Operator

01-19-~~44~~16 Sonoran Natl Mon. Substantial "Cirrus Blanket"
1415 0 Light 40 26°C ~~30°C~~ 4-NE 8% 1000' 40
Substantial Ground Haze / Occlusion in immediate & surrounding area.

* * 01-19-~~15~~16 S.N.M Same Conditions @ 1415
1445 0 Light 45 26°C 4-NE 5% 1000' 30

01-19-~~15~~16 S.N.M
1515 0 Light ~~59~~ ~~50~~ 52 25° 5-NE 5% 1000' 30mi

Health Index is 6

01-19-16 SNM
1525 0 Light ~~54~~ 57 25° 5-NE 5% 1000 30mi.

PM 2.5 # 4

~~Identification of Unknowns~~

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Phenyl Salicylate $C_{13}H_{10}O_3$

01-19-16 SNM Same Condition
1630 0 None 36 24°C 4-NE 9% 1000' 30'

S.N.M
1730 0 None ~~4~~5 19°C 1-N 21% 1000 30mi

S.N.M
1800 0 None 2 17°C 1-N 32% 1000' 30mi

~~1900~~ 01-19-16 S.N.M. "Cirro-Stratus" Blanket
1900 0 None 2 15°C 0-NA 43% 1000' 30mi

white
01-20-16 S.N.M Clear, Weak diffuse sky haze color,
0845 0 ~~Lig~~ None 2 15°C 4-S 34% 1000' 60

medium & to N in Phoenix area.
01-20-16 S.N.M. Mostly Clear, Aerosol Haze to South, Light Haze Overhead
1130 0 ~~None~~ Light 6 26° 2-S 11% 1000' 60

& South
01-20-16 S.N.M Mostly Clear, Haze to North (Phoenix area)
1215 0 ~~Mod~~ light ~~25~~ 20 28°C 4-N 19% 1000' 50

01-20-16 S.N.M Mostly Clear; Diffuse Haze In all quadrants & Overhead
1400 0 Light 20 27° 2-S ~~20~~ 14% 1000' 50

approaching
01-20-16 S.N.M Mostly Clear · Improving Visibility towards sundown
1700 0 Light 23 [illegible] 28°C 3-N ~~18~~ 16% 1000' 60

01-20-16 S.N.M Same Conditions as Previous, Sundown in place
1745 0 Light ~~2~~3 18°C 1-N 31% 1000' 65

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Date Location State Weather
~~Potassium Iodide~~ KI
Time Pop Vis Traffic PM T° Wind Dir % RH Elev Vis

Moderate
01-21-16 S.N.M Clear, but Aerosol Trails to NE (Phoenix area)
Moderate & SE (Tucson area) & moderate overhead
1700
0 0930 0 Medium 2 16° 2-N 40% ~~1700~~' 60

01-21-16 S.N.M Increasing Haze Cover, Aerosol Trails
4 1115 0 Medium 32 25C 4-N 11% 1700' 50

~~1530~~ 01-21-16 S.N.M. Mostly "Cloudy" Cirro Stratus Blanket, Haze
1530 0 'Light 12 25°C 3% [illegible] 1700' 50m
5-E
15%
0 1730 0 Light 2 22°C 0-NA 1700 60
Partly Cldy - Diffuse Cirro-Stratus.
No significant haze @ ground level, S.N.M. 01-21-16
Broad-Scale Cirro-
01-22-16 SNM Mostly Sunny; Substantial Diffuse Stratus Haze
0 1030 0 Medium 2 22°C 4-E 7% 1700' 60

01-22-16 SNM Same Substantial Broad Scale Diffuse Cirro-Stratus
1 1145 0 Light 11 26°C 8-E 6% 1700 60'
Modest ~~No significant~~ ground haze
01-22-16 SNM Same: Substantial Broad Scale Diffuse Cirro Stratus
1 1430 0 ~~None~~ Light 12 27°C 3-E 5% 1700' 60'

01-22-16 SNM Mostly Sunny, Diminished but Visible
Diffuse Cirrostratus Layer.
0 1600 0 Light 2 23°C 3-E 6% 1700' 60m

01-22-16 SNM Diffuse Cirro Stratus Layer, 60% Coverage
0 1830 0 Light 2 19°C 0-NA 21% 1700' 60m

PM2.5 #5

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Health Index ~~Sodium Chloride~~ ~~NaCl~~ S.N.M Operative

01-23-16 Mostly Cldy, Dense Cirro Stratus Layer, Active Aerosol ~~[illegible]~~
Ø 0900 Ø Medium 2 16°C 2-SW ~~[illegible]~~ 24% 1700' 60

01-23-16 S.N.M. Dense Cirro Stratus Layer - Partly Sunny
4 1245 Ø Light ~~[illegible]~~ 40 27°C 2-NE ~~[illegible]~~ 4% 1700 50

01-23-16 SNM Stratus, Cloudy.
3 1445 Ø None (Visible) 25 29°C 2-NE 6% 1700 45

0 01-24-16 SNM Clear, some Cirro-stratus to S-SW.
0830 Ø None 2 16°C 1-W 33% 1700 65

0 01-24-16 SNM Clear, Some Cirrostratus to S-SW
1000 Ø None 2 19°C 4-W 19% 1700 65

01-24-16 SNM Clear, Some Cirrostratus to S&SW
Ø 1300 Ø None 5 25°C 6-W 9% 1700 65

01-~~25~~ 24-16 SNM Clear
Ø 1600 Ø None 5 26°C 7-NW 4% 1700 70

01-25-16 SNM Mostly Cldy, Cirro Stratus, Some Mare's Tails
Ø 0930 Ø None 2 16°C 1-W 24% 1700 70

01-25-16 SNM Partly Cldy, Diffuse Cirro-Stratus to S&W.
Haze layer visible to NE over Phoenix area. Mildly diminished visibility.
1 1300 Ø None 10 27°C 2-NE 6% 1700 55

01-25-16 SNM Mostly Clear, Cirro Stratus Bank to S, Mild Haze to NE
Ø 1415 Ø None 2 23°C 4-W 13% 1700 60

PM2.5 #6

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Identification of Unknown

Date Location State Weather

Sucrose ~~C12 H22 O11~~

Time Pop Vis Traffic PM T° Wind-Dir %RH Elev VS

01-26-16 SNM Clear
0 0900 0 None 2 15° 3-NE 14% 1700 ~~80~~ 80

01-26-16 SNM Clear
1430 0 None 2 ~~26°C~~ 24°C 8-NE 2% 1700 80

01-26-16 SNM Clear
1800 0 None 2 16°C 0-NA 12% 1700 80

01-27-16 SNM Clear
ok ✓ 0945 0 None 2 19°C 4-NE 8% 1700 80

~~01-27-16 SNM Clear Mo Sunny Overhead / Diffuse & NW CirroStratus to W, mild Haze~~
✗ ~~1215 0 None Light 22 27°C 5-NE 7% 1700 70~~
~~This reading does appear to be anomalous and will be removed.~~
Discard → ~~Immediately prior the meter fell onto ground &~~
~~roadway dust may be interfering w/ reading~~
The data point is not consistent & will be discarded

01-27-16 SNM Mostly Clear, Increasing Diffuse Cirro
Stratus bank to W & N.
ok 1530 0 None 2 21°C 3-NE 5% 1700 70

Sundown occurring 01-27-16 SNM 50% Cirrostratus, Diffuse Haze bank from W extends to overhead. Increasing, Increasing Aerosol/Traffic
1745 0 Light 10 20°C 1-NE 7% 1700 60

Identification of Unknowns

We know that compounds that do not melt easily & that conduct are likely to be ionic.
Why? Are ionic bonds strong? We know why they conduct. Ionic compounds are likely to be soluble in water.

We saw that 3 compounds:
$CaCl_2$
KI } satisfy these criteria
NaCl
soluble in water
conductive
do not melt easily.

so we conclude that these are likely ionic compounds.
Does that mean everything else by default is covalent?
It does seem that way, but that does not seem to be reasoning very much.
Question: how does the structure, bond type, ~~ethanol solubility~~ affect the melting point?
What is it that affects the melting point?
What about the geometry? Can you predict the geometry?

Page 231 Identification of Unknowns

Jan 15 ~~2015~~ 2016

$FeSO_4$:

We have the question as to why it is acidic

One person gave us the dissociation as

$FeSO_4 + 2H_2O \Leftrightarrow 2H^+ + SO_4^{2-} + Fe^{2+} + 2OH^-$

He says lots of H^+ and little OH^-
but this does not seem correct.

From another source:

$4Fe^{+2}(aq) + 4H^+(aq) + O_2(aq) \rightarrow 4Fe^{+3} + 2H_2O$

a pH of 4 or lower will stabilize Fe^{2+} and will actually favor the reduction of Fe^{3+} even in the presence of atmosphere O_2. The result is a solution that is practically all ferrous sulfate.

Acidic solution stabilize Fe^{+2}

Identification of Unknown
Stronger section (S.S.)

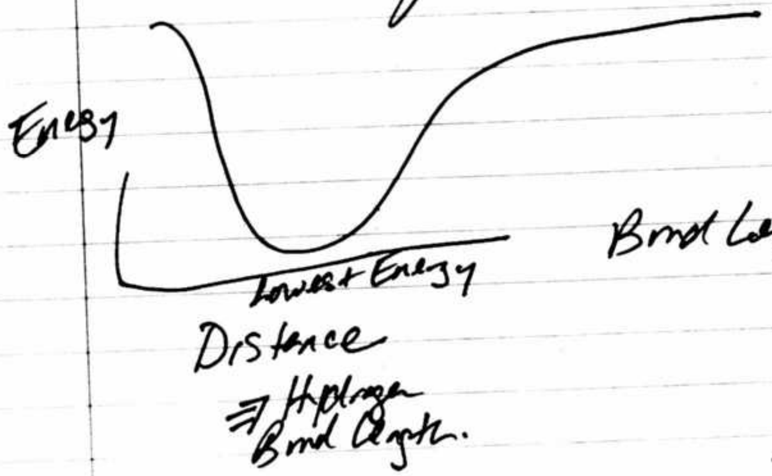
Jan 15 2016

Continuing w/ ChemLab Bond Lab & Zumdahl p 349
Ionic substances form with one atom that has a high affinity for electrons (ie high electronegativity) and an atom that loses electrons easily (ie low electronegativity and it would also seem a low ionization energy.) – is this true?
Clearly from Zumdahl p326 this certainly is the case. Group 1 has very low ionization energies, Group 0 has very high ionization energies.

And ultimately it is about seeking a configuration with a lower energy state. NaCl joined has a <u>lower</u> energy state than when the ions are separated.

Now, away from ionic bonds

Two hydrogens form a covalent bond



This is a picture of a covalent bond.

And then when they are asymmetrical you have a <u>polar</u> covalent bond.

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Identification of unknown (S.S.)

Our next big question is headed towards solubility / Why do some things dissolve in water but not alcohol, or visa versa

Zumdahl has a very good discussion on solubility, once again from the perspective of energy & energy state. Let's take our time through this Starting p 515.

Solutions can actually be SOLIDS! GASES! and liquids. Zumdahl will now take on the question of <u>why</u> "like dissolves like"

recalling

And now we have learned what is actually affecting bonding (electronegativity & ionization potential, primarily) to create

1. Ionic bonds
2. Covalent bonds
3. polar covalent bonds.

Remember our chart for bonds $<.6$ covalent

$.6-1.4$ polar covalent?

This is from memory >1.4 ionic

~~Check it~~.

Now go back to the <u>why</u> of "like dissolves like".

He looks @ it from a heat perspective. It requires energy to expand both the solute (incoming) and the solvent (receiving) and energy is released in the actual interaction or mixing process.

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Identification of Unknowns (5.5)

So the answer to like dissolves like is because to do otherwise it requires too much energy.

"Processes that require large amounts of energy tend not to occur".

And now we talk about structure and solubility. There should be a direct relationship.

We have talked in terms of heat & lower energy states. We have talked about expansion of both the solute & the solvent, and the mixing or interaction of them both. We have talked about bonding forces (ionic, covalent & polar covalent). We have talked about ionic substances & conductivity.

* Remember our three foremost measurement characteristics were melting point, solubility (both alcohol & water, and even more non polar substances for that matter) and ~~solubility~~ conductivity.

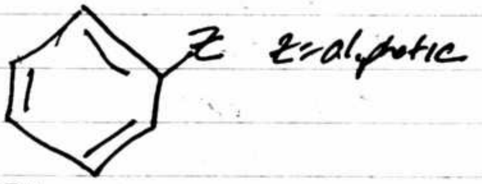
We are making some progress as we step through these.

Now we are working into structure.
We have something here. Polar vs non polar structure is the key. Vitamins are given as the example. Eg Vit A is largely non-polar (soluble in fats & oils, can accumulate) vs eg Vit C is water soluble, does not accumulate.

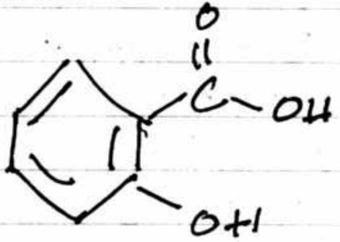
Page 235 Identification of Unknowns
(55)

I wonder what phenyl salicylate looks like? We know that it has a benzene ring attached to some aliphatic forms, it would seem.
Notice that it is insoluble in water but soluble in alcohol. This makes sense.

Salicylic Acid is aspirin.
It also has a phenyl group upon it so phenyl salicylate should certainly have some similarities to aspirin



Phenyl

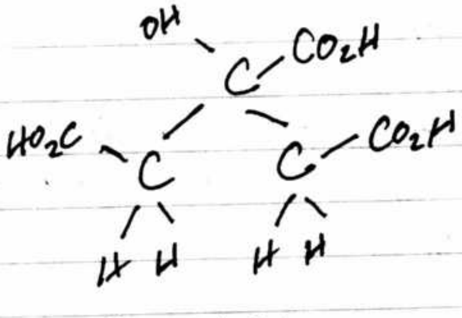


Aspirin
Salicylic Acid

We anticipate phenyl salicylate to be a cross between these two. We see that it has both polar and non polar components to it. This apparently shifts it enough to be soluble in alcohol but not water. This makes sense. We also see that the melting point is the lowest of the group. So what does this mean? It should mean that the bonds are weaker than the ionic substance (which we know to be the case) and even citric acid.

Identification of Unknowns (5.5)

What is the structure of citric acid, for comparison of bond strengths?



from McMurray, India

Presumably this take more energy to break down than for phenyl salicylate.

Citric Acid

all from McMurray p 125-6

C-C	347 kJ/mol	C=C	614
C-H	413	C=O	745
C-O	358	O-H	467

also from Zumdahl p 372

Making product bonds releases heat
Breaking reactant bonds absorbs heat } Somewhat counter-intuitive?

"Exothermic reactions are favored by stable products w/ strong bonds and by reactants w/ weak, easily broken bonds".

Zumdahl p 361: "Bonds result from the tendency of a system to seek its lowest possible energy"

Jan 16 2015

Now we get to return to Crippen's Book!
Identification of Organic Compounds w/ the Aid
of Gas Chromatography.

This really is one of my favorite books, which
was almost destroyed & lost in the NM Blizzard.
This really is an amazing book.

Every chapter is incredibly valuable.

1. Intro
2. Preliminary Examination
3. Solubility!
4. Physical Properties!
5. Functional Group Tests

How more perfect can you get?
The only weakness here is that it assumes
that it is organic. How would you know if
something is organic or not? It seems like
burning it is the most obvious method.
But diamond won't burn. So this does not
seem to be absolute, but it does seem to be
a good start.

Well, on the net there is no absolute test to
determine if something is organic or inorganic.
From a practical standpoint, one definition of a
organic compound is that it has

"a carbon "backbone" w/ some hydrogens attached"

Page 238

Some folks seem to try and use a purist definition that it only needs to contain carbon, such as CCl_4 - carbon tetrachloride.
This certainly does seem questionable to me as well as the diamond example. It seems to me that something that is organic does contain carbon but that it is also a biomolecule of some kind. The definition does indeed seem to ultimately be arbitrary.

Also, ultimately, it seems like the best test is one of burning. Does it decompose during combustion?
So we will have to go with this and assume that it does decompose. Organophosphates are a great example - as you recall they have ester functional groups.

Now we can proceed w/ Copper.
Intro chapter first. (You can always be thinking of your bond lab in the background
$CaCl_2$, Citric Acid, Phenyl Salicylate, KI, NaCl, Sucrose
↑ ↑ ↑ ↑
Inorganic organic organic Inorganic Inorganic, Organic
3 Inorganics, 3 Organics, this is a great representative set. In this case the inorganics happen to be ionic, but this is hardly always the case.

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In the introduction, Crippen give a general flowchart. We only have the means & knowledge to use a portion of the table.

We now go to the preliminary examination section. This is a little bit more practical in its approach.

this section is more practical than this

The first goal seems to be purification of the sample, ie, most likely distillation if it is a liquid or crystallization if it is a solid. Crystallization should be a great process to try in a Chemlab to look for.

Pyrolysis p17-18 Burning a sample can give many clues as in Table 2-2.

Solubility Chart is very useful on p42
But to even get started you need Ether.
Where do you get ether?

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Jan 17 2016 Sunday

[redacted]

In addition to Palmsens I would like to
1. look @ a Chemlab for crystallization
2. Study Cropper - esp. solubility. - a great book

w/ Palmsens there are many capabilities, including:

Voltammetry: Name Only
EM 104 1. Linear Sweep Voltammetry TE P135 (EMP104)
EM 90 2. Differential Pulse " ET P58 ET 67
3. Square Wave " ET P60 EM116
EM p85 4. Normal Pulse " ET P57 & Stripping
5. AC " ET P63 Voltammetry
6. Cyclic " ET P62 for each
EM99 7. Stripping Chronopotentiometry

Methods as f(t)
ET132 1. Amperometric Detection
2. Pulsed Amperometric Detection
3. Multiple Pulse Amperometric Detection
4. Fast Amperometry
5. Potentiometry
6. Open Circuit Potentiometry
7. Multistep Potentiometry
8. Multistep Amperometry

EIS: Impedance Spectroscopy
1. Potential Scan, 2. Fixed potential, 3. Time Scan

We have two topics of interest right now.

1. Voltammetry techniques

   Two of the India books are superior
   Electroanalytical Technique - Laksh
   Electroanalytical Methods - Rani

2. Solubility - Crippen is marvelous

& the two Chem textbooks will also be helpful on general chemistry.

3. You are also interested in Chemlab - anything on crystallization.

Chemlab has a fractional crystallization lab and a Redox Titration lab. Very good.

Let us start w/ basic voltammetry.

Notice w/ EM - Rani p 104 he specifically says that linear sweep voltammetry can be applied to any stationary electrode including Carbon.

Our calibration run w/ distilled water looks like Rani p 105 (c).

But our plot of a metal salt in solution looks more like Rani p118 which is "stripping voltammetry".

Stripping voltammetry is more sensitive because apparently you have a higher peak height. The question is what was done to generate the higher peak height, since we seem to be doing that. We are definitely looking @ the derivative of the situation.

So lets start out by looking @ the differences between various forms of voltammetry, including what is called stripping voltammetry.

$\frac{mg}{liter} = \frac{?}{million}$ $\frac{1E\text{-}3gms}{1000ml} = \frac{1}{1,000,000}$ or $\frac{mg}{liter} = PPM$

Voltammetry can reach parts per billion.
From Amel in Bluefire:
Linear Sweep Voltammetry has a detection level of mg/L.
This is exactly where we are.

Cyclic Voltammetry is a type of Linear Sweep Volt (LSV).

$E_0 = \frac{E_{pa} + E_{pc}}{2}$ pa = Peak @ anode
pb = Peak @ Cathode

This is exactly what we are doing, except plot is w.r.t. time

Interesting, but if you interject a pulse signal on top of what we are doing, you can increase sensitivity by a factor of 10 to 100.
This would mean .1 PPM to .01 PPM
which is 100 ppb to 10 ppb. This would be superb.
This is called Differential Pulse Voltammetry.
Another variation is square wave voltammetry.

Differential Pulse Voltammetry &
Square Wave ~~Pho~~ Voltammetry
are both methods that increase the
sensitivity of Linear Sweep Voltammetry.

Stripping Voltammetry also increases the
sensitivity. It can go down to 1PPB.
It requires a Concentration phase but I am
not sure how this is done.

Polarography uses mercury.
We are not likely to do this.

Summary of Voltammetry

* Every oxidizable or reducible substance that
can be dissolved in an appropriate
solvent can be analyzed by Voltammetry.
* The main application of voltammetry is the
trace analysis of heavy metals in water,
food, soil, agri product, pharmaceuticals,
biolgy biology, etc

Interesting comment on the periodic table.
He says Group I & Group II elements can only
be detected if they are alone in solution?

!!! Amel P23 Bluefire gives a chart &
table of detectable elements and anions
and there are a lot of them!

and functional groups

Amel says on p 24 that Group I & Group II elements cannot be analyzed w/ voltammetry.
I do not believe this ????

Kounaves p 711
All voltammetric techniques can be described as some function of E, i and t.

Voltammetry is an "active" technique.
Potentiometry is a "passive" technique.

Jan 18 2016

This will be an experiment in conductance & titration.

We are starting out with distilled water. TDS = 0. PPM
Vol = 83 ml.

We are letting pH meter settle.
pH meter has settled from ~10.0 to 7.9

5 drops of lemon juice added.
TDS still shows nothing. This is not good.
pH meter is settling to 5.0
Test TDS meter in salt.

The TDS meter appears to be shot.
We will have to use pH alone.
We start w/ 20 ml of ~~1.0M NaOH~~ H_2O
we add 5 drops of 1.0M NaOH (.06 ml per drop)
What is our molar concentration now of NaOH.

Now calibrate pipette.

$$\frac{95\ \cancel{45}\ \text{drops}}{5\ \text{ml}} = \frac{1\ \text{drop}}{X}$$

X = ~~0.11 ml~~ .05ml
≈ ~~0.10 ml~~

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Looks like a good job.

Now Titrate

NaOH dilute

Drops from Pipette	pH	pH*
0	5.0	3.0
4	5.1	
40	5.2	
60	5.3	
80	5.4	
90	5.5	
100	5.6	
110	5.7	
120	5.8	
132	6.0	4.0
150	6.2	
160	6.4	
170	6.5	
180	6.6	
190	6.8	
200	7.0	5.0
210	7.2	
220	7.4	
230	7.6	
250	7.8	
260	8.0	6.0
280	8.3	
290	8.6	
300	9.0	7.0
310	10.2	8.2
320	11.0	9.0
330	11.3	9.3
340	11.5	9.5
350	11.6	9.6
360	11.7	9.7

pH of raw lemon juice stated to be about 2.0

Ka of citric acid is 7.4E-4

Raw lemon juice from bottle has a pH of 4.3

Seems to me that pH values should be decreased by approx -2

This is real life titration data. Not theoretical. Now that you have it, what do you want to do with it? The real question of course, is, how strong is the concentration of citric acid? So this is a real life example.

Another question could be, based upon all the work that you have done, is ask what is the pKa of citric acid?

First of all, what is the conc. of the NaOH you are using? You have a dilution.

You start out with 20 ml H_2O
We add 5 drops 1.0M NaOH (1 drop = .06 ml)
5(.06 ml) = 0.30 ml

$$\frac{.30\text{ ml NaOH (1M)}}{23\text{ ml } H_2O} = \frac{13.04\text{ ml (1M)}}{1000\text{ ml}} = .013\text{M NaOH}$$

Eg. 10 ml of 1M solution added to 100 ml =

$$\frac{10}{110} = .09\text{M solution} \qquad \frac{10\text{ ml of 1M}}{90\text{ ml} + 10} = \underline{\underline{0.10\text{M}}}$$

I think this assumes total dissociation

$$C_aV_a = C_bV_b$$

$$C_a = \frac{C_b \cdot V_b}{V_a} = \frac{(.013\text{M})(310\text{ ml})}{83.25\text{ ml}} = \underline{\underline{.048\text{M}}} \text{ ????}$$

← equilibrium point is reached here.

[83 + 5(.05) ml = 83.25]

Does this work for weak acid - strong base combinations? You are back to basic questions.

Back to the drawing board on all of this. Actual vs Theory? Practice vs Demo.

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Look @ what the EPA has done here!

PM2.5	AQI
0	0
12	50
12.1	51
35.4	100
35.5	101
55.4	150
55.5	151
150.4	200
150.5	201
250.4	300
250.5	301
500	500

Health Index	PM2.5		PM2.5/AQI	AQI		
1	0			0		0
2	6		24%	25		4.17
3 4	23.75	45.45	31% 36%	75.5	125.5	3.18 2.06
~~4~~ 5	102.95		59%	175.5		1.70
~~5~~ 6	200.45		80%	~~400.5~~	250.5	1.25
~~6~~ 7	375.25		94%	400.5		1.07

$$AQI = 5.73e^{-.288\,PM2.5}$$

$r^2 = 0.978$

MSE = 8.04 E-3

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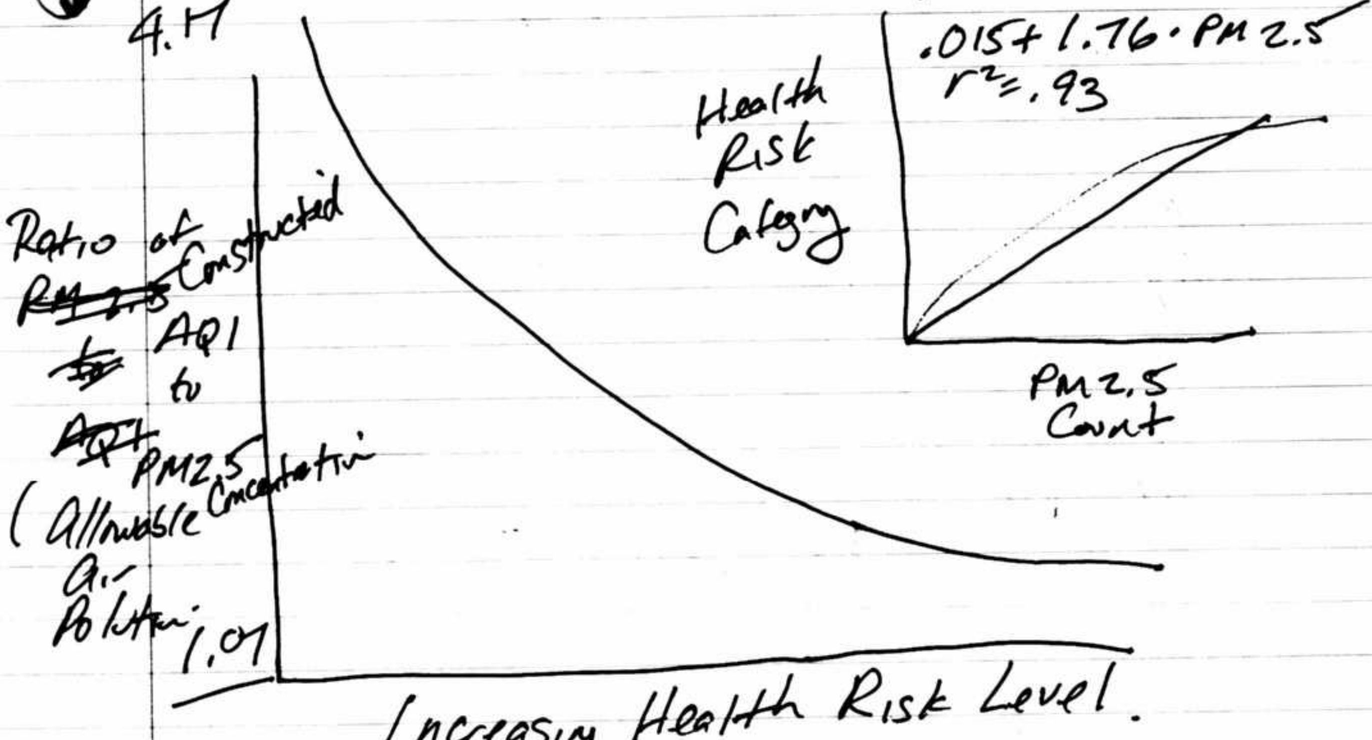
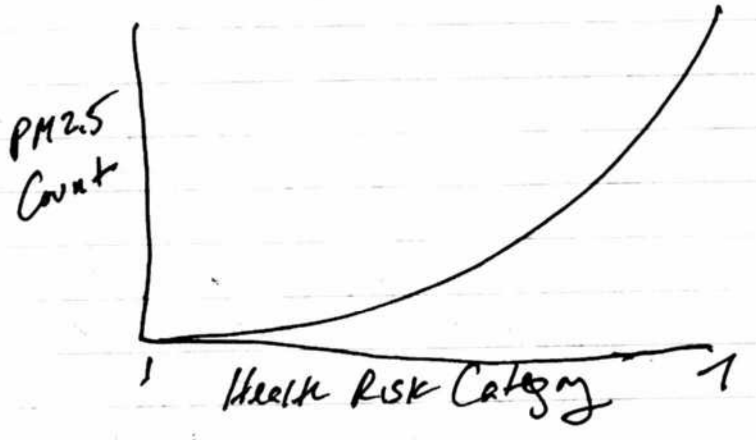
But logistic Curve is even better.



Health Risk ≈ $.015 + 1.76 \cdot PM2.5$

$r^2 = .93$



$$PM_{2.5} \approx \frac{1215.5}{1+621.8e^{-.804 \cdot \text{Health Risk Category}}}.$$

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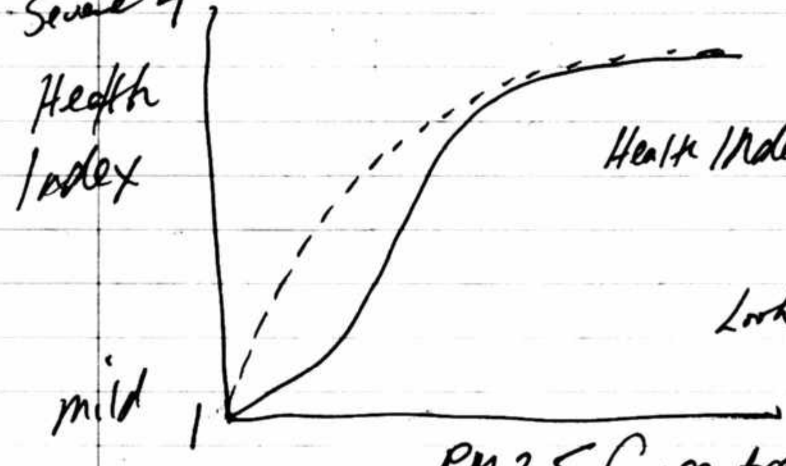
The Derivative is
what is important here

Logistic Curve is even better.



Health Index ≅

Look at derivatives

$$\text{Health Index} \cong \frac{7.04}{1 + 4.06e^{-.013 \cdot PM2.5}}$$

MSE = .05

So the Health Index is more severely impacted by the initial increase in PM Count.

EPA has skewed the index so that it diminishes the effect where the most likely pollution is likely to take place, and especially that from aircraft operations.

Now look @ how EPA handle the issue.

PM2.5	EPA Index	
0	0	1
6	25	2
23.75	75	3
45.45	125	4
102.95	175	5
200.45	250	6
375.25	400	7

Logisitic does not fit well MSE = 1335.8

They used a concave downward quadratic

$$y = -1.42E{-3}\, PM2.5^2 + 1.51\, PM2.5 + 26.3$$

$r^2 = 0.98$

PM = 0 to 400

$y' = -2.84E{-3}x + 1.51$

$y'' = -2.84$

Can we plot

$\frac{\Delta \text{Health}}{\Delta \text{Concentration}}$ @ 30, 40, 50 PM

Logistic

X	y'
20	.0169
30	.018
40	.019
50	.02
75	.022

EPA Quadratic

X	y'

Jan 20 2016

We see now that we have 3 different scale of measurement in place:

1. Actual concentration levels (avg or max or short-term exposure comes into debate.

2. EPA AQI (1-6)

3. Omega (1-9), But also actually ~~1-6~~ 1-5

Let's try and equate them

$\overline{\text{PM2.5}}$	$\overline{\text{AQI}}$	AQI verbal	Omega
0	0	GOOD	0
6	25	GOOD	0
23.75	75	MODERATE	3
45.45	125	SENSITIVE	4
102.95	175	UNHEALTHY	9
200.45	250	V. UNHEALTHY	9
375.25	400	HAZARDOUS	9

$\overline{\text{PM2.5}}$ ~~Omega~~	Omega	Omega6		
3	0	1	100	9
10	1		200	9
16	2		300	9
25	3		400	9
39	4		500	9
48	5			
56	6			
72	7			
81	8			
90	9			

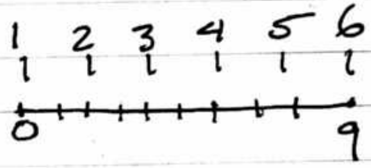
Omega is a log scale

Omega's evaluation of air quality is closer to a log function.

Omega Air Quality Index $\cong -2.97 + 2.17 \ln(PM2.5)$

0-9 Scale $r^2 = 0.87$

Now Compress to a 1 to 6 scale

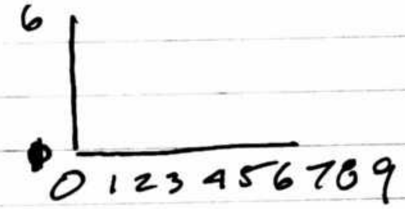


Take omega alone

0 - 9 ⇔ 1 - 6

so first add 1 (omega + 1) this gives 1 - 10

and then multiply by 6/10



so

~~Omega~~ So ([illegible] $\left(\frac{x}{9}\right)$ [illegible]

3

PM2.5	Omega	Omega6	Omega verbal
3	0	1	Very Good
10	1	1.2	Good
16	2	1.8	Mod
25	3	2.4	Mod
39	4	3.0	Mod
48	5	3.6	Poor
56	6	4.2	Poor
72	7	4.8	Poor
81	8	5.4	Poor
90	9	6	Very Poor
100	9	6	Very Poor
200	9	6	Very Poor
300	9	6	Very Poor
400	9	6	Very Poor
500	9	6	Very Poor

So

$Omega_6 = -.97 + 1.26 \ln(PM2.5)$

$r^2 = .86$

This equation kicks in @ PM 5.0 so this is decent

Therefore we see that omega calls anything above ~ 40 as being poor.

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<12 Green
13+ Yellow
35+ ~~[illegible]~~ (aqua)
55 Red

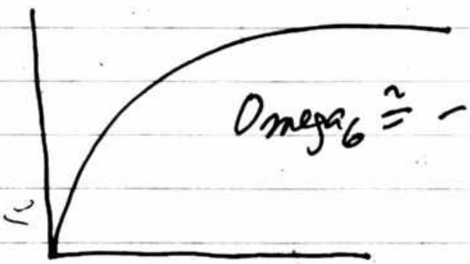
Omega health Index

0 — 7	0
8 — 12	1
13 - 20	2
21 - 31	3
32 - 46	4
47 50	5
52 60	6
72	7
80 82	8
~~[illegible]~~ 90	9

46 4
48 55 5
62 60 6
77 8

9 84+

We have learned that Omega
has a log scale
with poor air qualifying anywhere
above ~ 48 - 50.



$$Omega_6 \simeq -.97 + 1.26 \ln (PM2.5]$$

With a very steep influence in the lower
Concentration Changes.

Health Index

Jan 20
Now what does the EPA do, besides lie on their website?

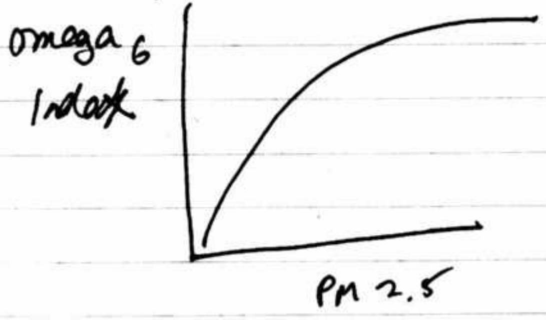
The EPA's scale is of the form

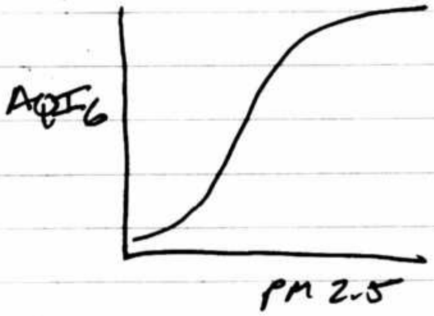
PM2.5	AQI	Verbal
6	1	Good
23.75	2	Moderate
45.45	3	Sensitive
102.95	4	Unhealthy
200.45	5	V. Unhealthy
375.25	6	Hazardous

The EPA curve is a logistic curve

$$AQI_6 \overset{\sim}{=} \frac{5.70}{1 + 3.11 e^{-.02 PM2.5}} \qquad \frac{C}{1+ae^{bx}}$$

MSE= 0.19





The ratio and the slopes are interesting topics

[illegible]

We therefore have a fundamental flaw in the scaling system that the EPA uses as well as inadequate or inaccurate information on the EPA website.

Is there any reason to think that the health effects are logistic vs logarithmic? Not likely?

$y = \frac{c}{a+e^{bx}}$ what is y'?

$y = c\cdot(a+e^{bx})^{-1}$ $\underline{de^{u}}$ $e^{u}\cdot\frac{du}{dx}$

so $y' = c\cdot(-1)(a+e^{bx})^{-2}e^{bx}\cdot b + (a+e^{bx})^{-1}\cdot 0$

$y' = \frac{-bc\cdot e^{bx}}{(a+e^{bx})^{2}}$ vs $y = a+b\ln x$

$y' = \frac{b}{x}$

If $y(x) = \frac{1}{1+e^{-x}} = (1+e^{-x})^{-1}$ $y' = (-1)(1+e^{-x})^{2}e^{-x}\cdot(-1)$

then $y'(x) = (1+e^{-x})^{-2}(-e^{-x}) = \frac{e^{-x}}{(1+e^{-x})^{2}}$ $\underline{\text{OK}}$ $\frac{e^{-x}}{(1+e^{-x})^{2}}$

so I think you are on the right track there.

So what does this graph look like? $y = \frac{c}{(a+e^{bx})}$

$$y' = \frac{-b \cdot c \cdot e^{bx}}{(a+e^{bx})^2}$$

$a = 3.11$
$b = -.02$
$c = 5.70$

So

$$y' = \frac{.02(5.70)e^{-.02x}}{(3.11+e^{-.02x})^2} = y' = \frac{.114e^{-.02x}}{(3.11+e^{-.02x})^2}$$

A suitable graph is $0 < x < 500$
$0 < y < .01$

And we can see here that the role of $\frac{\Delta \text{ Health Index}}{\Delta \text{ Concentration}}$

is diminished quite strongly from PM2.5 of 0 to 100
exactly where we need to measure it most.

When a in Omega the derivative is

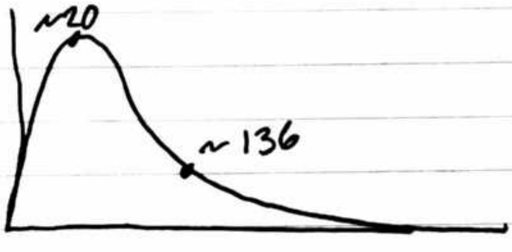
$$\frac{1}{x} \cdot b$$

Set Graph @ $0 < x < 500$
$0 < \frac{y_1'}{y_2'} < .02$

The ratio of the derivative is especially interesting.

$$\frac{\left(\frac{\Delta \text{ Health Index AQI6}}{\Delta \text{ Concentration}}\right)}{\left(\frac{\Delta \text{ Health Index Omega}}{\Delta \text{ Concentration}}\right)} = \frac{\Delta \text{ Health Index AQI6}}{\Delta \text{ Health Index Omega6}}$$

$\frac{y_1'}{y_2'}$



Jan 24 2016

Lets look @ integration instead in addition to the derivative

Omega6 $= -.97+1.26\ln(PM2.5)$ $\int$

AQI6 $\bar{x} = \dfrac{5.70}{1+3.11e^{-.02(PM2.5)}}$ $\int$

			Omega Health Index			
1-5	1.2	very good	0		5.80	+383%
1-10	8.9		0		13.6	+53%
1-20	33.1		1		30.8	-7%
1-30	63.9		2		50.6	-21%
1-40	98.9		2		73.0	-26%
1-50	137.2	moderate	3		98.1	-28%
1-75	243.0	↑	4		173.5	-29
1-100	359.5	↓	5	↑ 6	265.9	-26%
1-150	614.7	Poor	7	↓	491.8	-20%
1-200	891.4		9		751.6	-16%
1-300	1489.2		9		1308.0	-12%
1-400	2129.9		9		1876.	-12%
1-500	2802.4		9		2445.0	-13%

you used an average / [illegible] weight [illegible]

$$\int a+b\ln(x)\,dx$$

$$= bx\ln(x)+ax-bx$$

$$\int \frac{a}{1+be^{-cx}}\,dx$$

$$= ax + \frac{a\ln(|b\cdot e^{-c\cdot x}+1|)}{c}$$

so indeed it is a bit complicated.

H561e0W2$

6 Rating (Highest Achieved) w/ Known Aerosol Operators

From Good To ~~Poor~~ is:

Average underweighting is

$$\frac{383(0)+53(0)-7(1)-21(2)-26(2)-28(3)-29(4)-26(5)}{\cancel{383+53}\ 1+2+2+3+4+5}$$

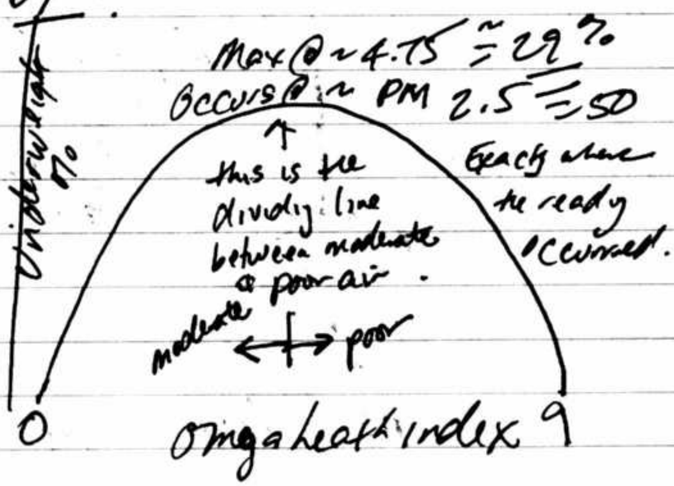
~~-26(5)~~

$= -25.3\%$ Underweighted Health Impact

The problem here is that underweights @ a health level of 4 has greater impact than at a health level of 1.
How to express this.

$+5 \quad -6 \qquad \bar{x} = -.5$

$\dfrac{+5(1)-6(1)}{2} = \dfrac{-1}{2} = -.5$



Underweighting function then the form

Underweight % $\cong -1.06$ Omega Health Index^2 $+10.3$

Jan 24 2016

Lets look @ integration instead in addition to the derivative

Omega6 AQI6

$$= -.97 + 1.26\ln(PM2.5) \int \qquad \bar{X} = \frac{5.70}{1+3.11e^{-.02(PM2.5)}} \int$$

	Omega6		Omega Health Index		AQI6	
1-5	1.2	very good	0		5.80	+383%
1-10	8.9		0		13.6	+53%
1-20	33.1		1		30.8	-7%
1-30	63.9		2		50.6	-21%
1-40	98.9		2		73.0	-26%
1-50	137.2	moderate	3		98.1	-28%
1-75	243.0		4		173.5	-29
1-100	359.5		5	6	265.9	-26%
1-150	614.7	Poor	7		491.8	-20%
1-200	891.4		9		751.6	-16%
1-300	1489.2		9		1308.0	-12%
1-400	2129.9		9		1876.	-12%
1-500	2802.4		9		2445.0	-13%

you used an average undo-weight some how

$$\int a+b\ln(x)\,dx$$

$$= bx\ln(x) + ax - bx$$

$$\int \frac{a}{1+be^{-cx}}\,dx$$

$$= ax + \frac{a\cdot\ln(|b\cdot e^{-c\cdot x}+1|)}{c}$$

so indeed it is a bit complicated.

Jan 25 2016 Page 261

There is an analysis in place that shows the likelihood of manipulated se ad data presentation to the public.
Also of inadequate, incomplete, or misrepresentative information on public access sites.

We need $\frac{\Delta \text{ in health}}{\Delta \text{ in PM Count}}$

Daily Mortality $\frac{0.2 - 0.6 \% \text{ Mortality}}{10 \text{ ug} / \text{m3}}$

Long Term Exposure Cardiopulmonary Mortality 6 - 13% per 10ug / pm 2.5

WHO: Standard 10 ug/annual avg
25 ug/m^3 for 24hr mean
not to be exceeded for more than 3 days/year

"Even at relatively low concentrations the burden of air pollution on health is significant."

$$\frac{dM}{dc} = \frac{0.4\%}{10g}$$

So @ a minimum

$$\frac{dM}{dc} = a \text{ constant}$$

WHO

Therefore

$$\Delta M = a \cdot \Delta C$$

if $\Delta C = 50 \mu g$

$.4(5) = 2\%$ increase in mortality daily mortality

=

$$\frac{755}{20} = 37.75$$ "deemed safe"

WHO judges 500 to be more than 20 times the level of particulate matter in the air deemed safe.
NY Times Jan 12, 2013

From Wikipedia:

22% increase in ~~Cancer~~ lung cancer rate per 10 ~~ug~~ in PM10 (DOES NOT APPLY)

annual increase of 5 ug/m³ led to 13% increased risk of heart attacks.

This is PM10! Not appropriate

Now let's think this through.

100 people exist w/0 concentration.
.4% die on a daily basis with a 10ug/ increase

	People Alive	Daily People Die	Remain. Pop	Conc.-ug/m3
0	100			0
1		~~.00~~.4	99.6	10
2		.398	99.202	10
3		.397	98.805	10

So this mean $\frac{100}{.4} = 250$

This says in 250 days everyone is dead.

No of people alive = $100e^{-.004d}$ $r^2 = 1.00$
after 1000 days there is 1.83 people alive and the race is nearly extinguished.

After 173 days half of the population would be dead. Does that make any sense.

This makes no sense, it should be an annual rate -

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WHO:
"all-cause daily mortality is estimated to increase by 0.2 - 0.6% per 10 ug/m^3 of $\underline{\underline{PM_{10}}}$.

This is not PM2.5!

Long term exposure is ass. with increase in Cardiopulmonary mortality by 6-13% per 10ug of PM2.5
so
10-57 =

health effects short term ex
long term exposure of pm 2.5 is a higher risk factor for mortality.

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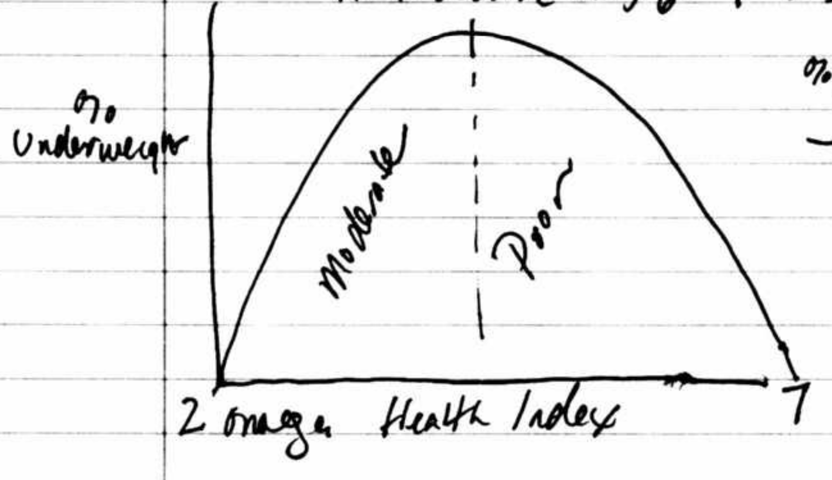
Band Integration

Omga$_6$ $= -.97 + 1.26 \ln(PM2.5)$

AQI$_6$ $= \frac{5.70}{1 + 3.11 e^{-.02 PM2.5}}$

PM2.5	∫	Δ % omga$_6$	OMEGA HI_{MID}		∫	ΔEV_6
1-10	8.9	+53%	0	1.5	13.6	0% ~~+53%~~
10-20	24.2	-29%	2	2.0	17.3	-12%
20-30	30.8	-36%	3	2.5	19.8	-22%
30-40	35.0	-36%	4	3.1	22.4	-28%
40-50	38.2	-34%	4	3.1	25.2	-32%
50-60	40.8	-31%	6	4.2	28.0	-33%
60-80	87.6	-26%	7	4.8	64.5	-33%
80-100	93.9	-20%	9	5.4	75.2	-30%
100-150	255.2	-11%	9	5.8	225.9	-21%
150-200	276.7	-6%	9	5.9	259.8	-12%
200-250	292.6	-6%	9	5.9	275.1	-20%
250-300	305.3	-8%	9	5.9	281.3	-5%
300-400	640.7	-11%	9	5.9	568.1	-4%
400-500	672.5	-15%	9	5.9	569.7	-4%

Max Occurs @ Omega$_6$ = 4 = 36%



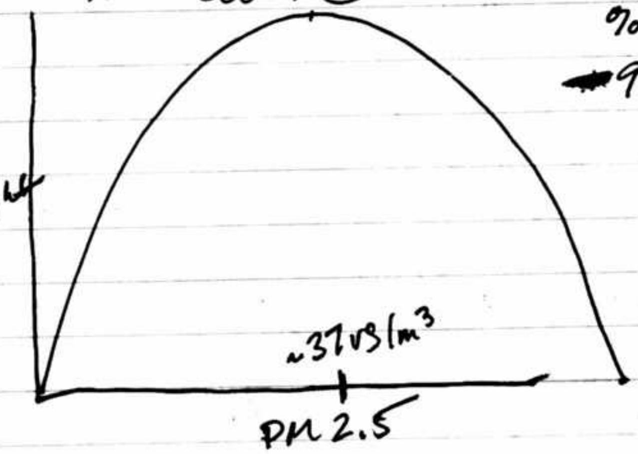
% underweight ≅

$-1.2x^2 + 10.2x + 14.4$

$r^2 = .90$

Max Occurs @ PM2.5 $\cong$ 37

% underweight $\cong$ $-9.7E{-3}x^2 + .72x + 21.7$



EV$_6$ % ∫ Underweight	Δ mean
13.6	+26%
19.7	-20%
25.3	-29%
31.1	-32%
36.9	-33%
42.1	-32%
96.5	-30%
107.3	-25%
281.3	-16%
294.3	-9%
295.3	-13%
295.5	-6%
591.0	-7%
591.0	-9%

This is exactly almost @ the max safe level.

Therefore @ the max safe level (i.e., the dividing line between moderate & poor air quality, the EPA underweights the ~~influence~~ health impact the most.

This analysis appears to be the most understandable;

Or in other words, when the influence is the most important, the data is underweighted the most.

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I have found another useful source of information:

airqualitynow.eu/about_indices_definition.php

PM 2.5 standards are listed as:

Index Class:

		1hr	Mid	24hrs
1	Very low	0-15	7.5	0-10
2	Low	15-30	22.5	10-20
3	Medium	30-55	42.5	20-30
4	High	55-110	82.5	30-60
5	Very High	110+	110	60+

Now the Hoang rating goes from 1 to 5
We need to extend it to 1 to 6
or even 1 to 9 to match Omega.

PM 2.5	EU_5 Scale	EU_6
0	1	1.2
15	1	1.2
15	2	2.4
30	2	2.4
30	3	3.6
55	3	3.6
55	4	4.8
110	4	4.8
110	5	6

a logistic fit works quite well to this

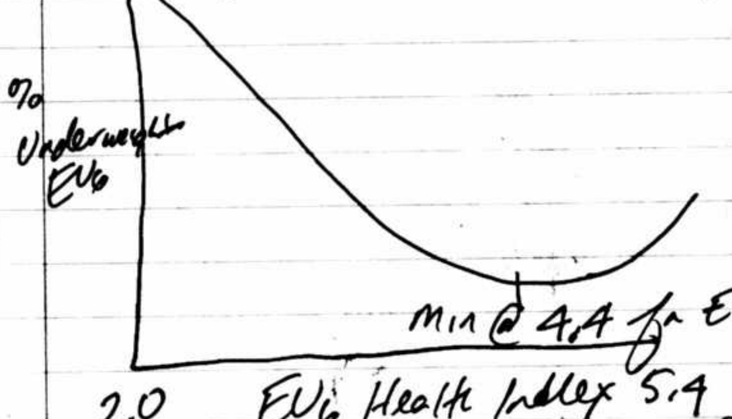
$$EV_6 = \frac{\cancel{3.64}\,5.91}{1 + 3.64e^{-.04 PM2.5}} \qquad Mse = 0.29$$

Now we will integrate in bands equivalent to $Omega_6$ and AQI_6 and populate the table.

Graph for EV_6:

$$\%Underweight = 3.76 EV_6^2 - 32.8 EV_6 + 37.6$$

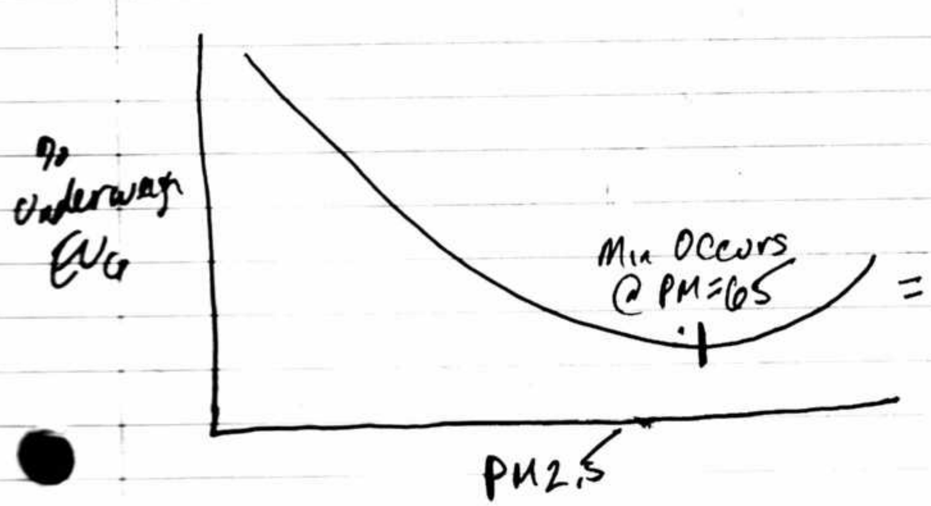
$$r^2 = .99$$



min @ 4.4 for EV_6 = −33.8% ≐ −34%

$Omega_6$ gave min @ −36%

Mean minimum occurs as −34%



Min Occurs @ PM=65 = −35%

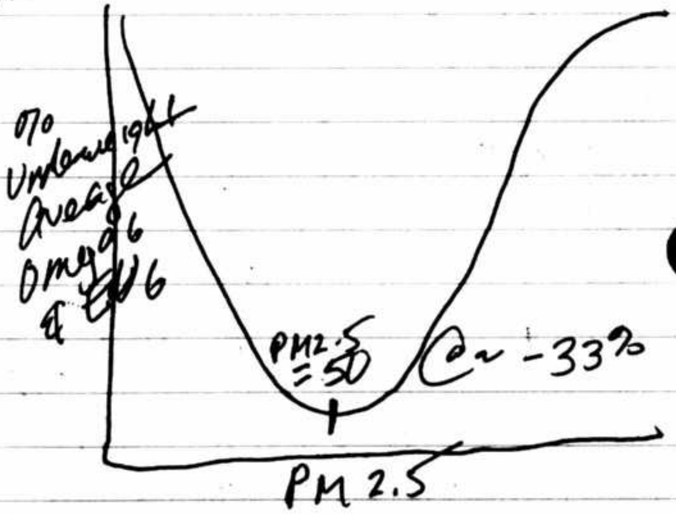
This means our average min occurs @

PM2.5 (37+65) / 2 = 51

≈ Avg Min occurs @ PM ≈ 50
and underweight factor ≈ 35%

Now, the final plot we would actually like to use is the averaged data. ≈

PM2.5	Avg Underweight
5	
15	-20%
25	-29%
35	-32%
45	-33%
55	-32%
70	-30%
90	-25%
125	-16%



~~Min occurs @ PM2.5 ≈ 60 @ -32%~~
A cubic actually fits this data much better
The min occurs @ PM2.5 ≅ 49.4 ≅ 50

with a max percentage of -33%.

$r^2 = 0.98$

$$\% \text{Underweight} \approx -6.98E{-5}\, PM2.5^3 + .02PM2.5^2 - 1.31PM - 5.2$$

Interestingly enough, the a quite close t the maximum reading obtained w/ actual aerosol operation on the ground thus far.

We need t round up all scales and put them in terms of PM2.5

Index$_i$ = f(PM2.5)

No, you actually do need t equate them.

PM2.5	* AQI$_6$	9 OMEGA	OMEGA$_6$	1 HR 5 EUR	EUR$_6$	* Mean: OMEGA6 + EUR6	(Mean OM$_6$+EU$_6$+UK$_6$	/ % ΔAQI$_6$	UK 10	UK 6
1-10	1	0	1	1	1	1	1.0	0%	1	1.0
10-20	2	2	2.1	1	1	1.6	1.6	+20%	2	~~1.4~~ 1.6
20-30	2	3	2.7	2	2.2	2.4	2.3	-20%	3	~~1.9~~ 2.1
30-40	2	4	3.2	3	3.5	3.4	2.9	-70%	3	~~1.9~~ 2.1
40-50	3	4	3.2	3	3.5	3.3	3.3	-10%	5	~~2.8~~ 3.2
50-60	3	6	4.3	3	3.5	3.9	4.0	-30%	7	~~3.7~~ 4.3
60-80	4	7	4.9	4	4.8	4.8	5.0	-20%	9	~~4.6~~ 5.4
80-100	4	9	6	4	4.8	5.4	5.6	-35%	10	6.0
100-150	4	9	6	5	6	6	6	-50%	10	6.0
150-200	4	9	6	5	6	6	6	-50%	10	6.0
200-250	5	9	6	5	6	6	6	-20%	10	6.0
250-300	5	9	6	5	6	6	6	-20%	10	6.0
300-400	6	9	6	5	6	6	6	0%	10	6.0
400-500	6	9	6	5	6	6	6	0%	10	6.0

66
32

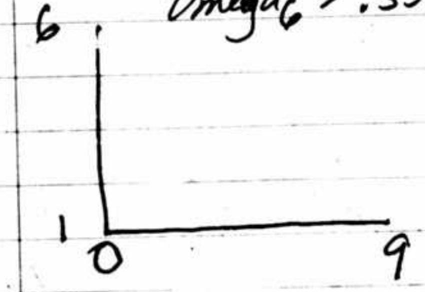
Translation: Omega_9 to Omega_6 $\quad$ Translation

0-9 ⇔ 1 to 6 $\quad$ Uk 1-10 ⇔ 1-6 Uk

so add 1 this brings from 1-10 $\quad$ $UK_6 = .444UK_{10} + .555$

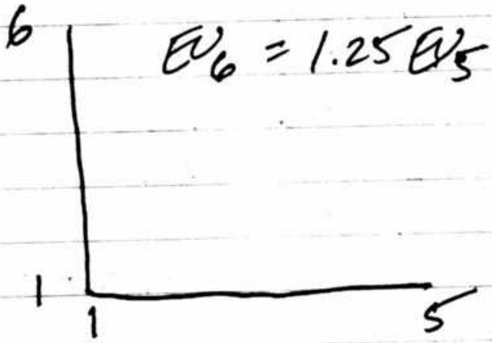
now multiply by 6/10

$$\text{Omega}_6 = .555(\text{Omega}_9) + 1$$



Translate EV_5 to EV_6 (1 hr)

$$EV_6 = 1.25EV_5 - 0.25$$



Analysis of AQI_6 data.
One could take it to be linear $r^2 = .82$ $Mse = .46$
But logistic is a better fit

$$AQI_6 := 5.57/\left(1 + 2.30e^{-.016PM2.5}\right) \qquad Mse = 0.27$$

$$\overline{\text{Mean}}\left(\text{OMEGA}_6 + EV_6\right) = \overset{6.01}{\cancel{4.73}}/\left(1 + 4.73e^{-.042PM2.5}\right) \qquad Mse = .04$$

$$\left(\overline{\text{Mean}}\ OM_6 + EV_6 + UK_6\right) = \frac{6.03}{\left(1 + 5.65e^{-.046PM2.5}\right)} \qquad Mse = .01$$

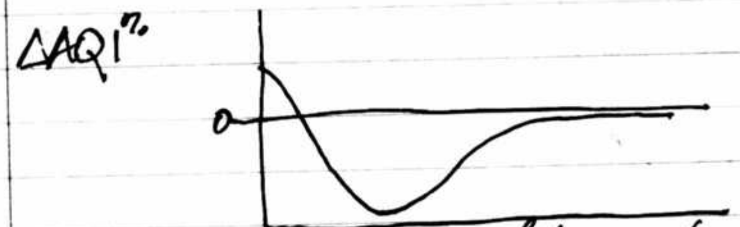
These are an exceptionally good fit.

You regained the exponential harmonic solution near Feb 2015. noted for the record.

It is called a basis function solution is a non-homogeneous diff eq. w/ constant coefficients.

Now lets integrate the two curves.

PM2.5	$\int AQI_6\, dPM2.5$	$\int OMEGA_6 + EUR_6\, dPM2.5$ mean	$\int OM_6+EU_6+UK_6$ Preferred	2way ΔAQI	% preferred	3-way % ΔAQI
1-10	16.1	11.4	10.1	+29%	+37	+42
10-20	19.8	17.1	15.8	+20%	+20	+27
20-30	21.9	22.7	21.6	-4%	+1	+8
30-40	24.1	28.8	28.3	-20%	-17	-18
40-50	26.3	35.0	35.2	-33%	-34	-27
50-60	28.5	40.9	41.5	-43%	-46	-39
60-80	63.6	95.8	98.0	-50%	-54	-47
80-100	72.1	108.2	110.4	-50%	-53	-46
100-150	211.7	291.9	295.0	-38%	-39	-32
150-200	243.7	299.4	300.8	-23%	-23	-16
200-250	261.7	300.4	301.4	-15%	-15	-8
250-300	270.7	300.5	301.5	-11%	-11	-4
300-400	551.8	601.0	603.0	-9%	-9	-2
400-500	555.9	601.0	603.0	-8%	-7	0



Min ~ 85 PM2.5

We have a beautiful solution w/ exponential harmonics

$$y = C_1 + C_2 e^{-\overset{*}{x}} + C_3 \cos(\overset{*}{x})\ C_4 \sin(\overset{*}{x}) + C_5 \overset{*}{x^2} + C_6 \overset{*}{x} \qquad X = \frac{x}{100}$$

4.1

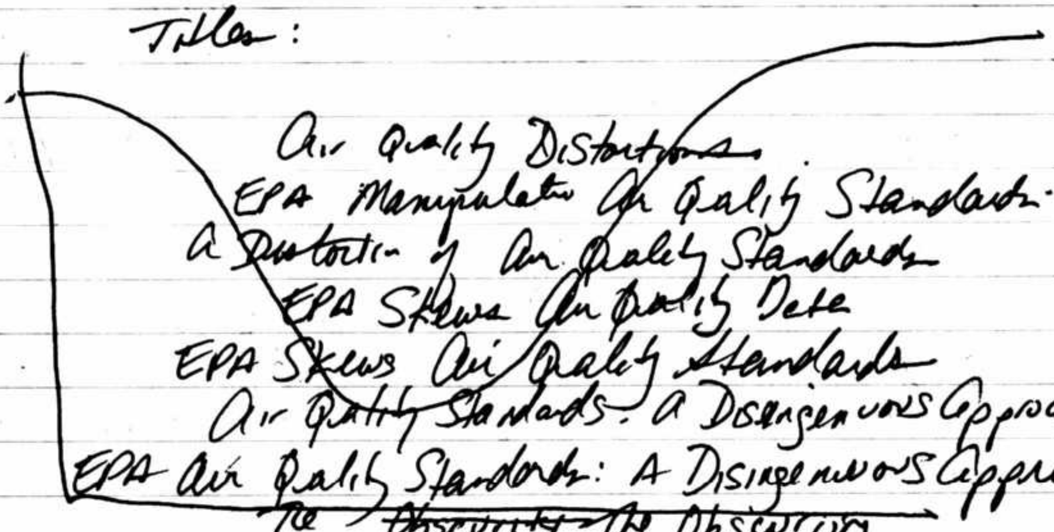
C_1	-895.3	-947.8
C_2	861.5	925.5
C_3	84.6	87.2
C_4	68.5	77.5
C_5	-61.1	-63.7
C_6	488.9	515.9

$\sigma = 3.6$

Looks perfect

Min @ approx 85UM

Titles:



Air Quality Distortions

EPA Manipulation Air Quality Standards:

A Distortion of Air Quality Standards

EPA Skews Air Quality Data

EPA Skews Air Quality Standards

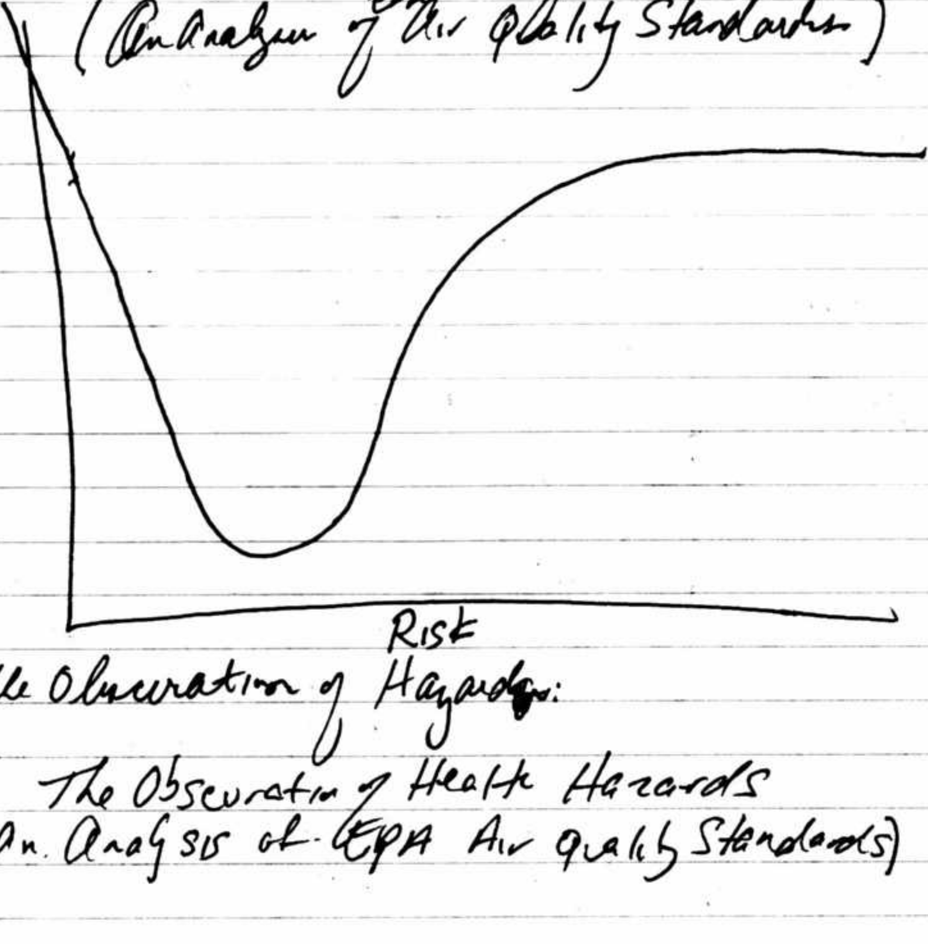
Air Quality Standards: A Disingenuous Approach

EPA Air Quality Standards: A Disingenuous Approach

The ~~Obscurity~~ The Obscuring

An Obscuration of Risk:

(An Analysis of EPA Air Quality Standards)



The Obscuration of Hazards:

The Obscuration of Health Hazards

(An Analysis of EPA Air Quality Standards)

I would like to form a comparison between the US + China.

	China AQI		US AQI
0-50	Excellent	0-12	Good
51-100	Good	12.1-35.4	Moderate
101-150	Lightly Polluted	35.5-55.4	Unhealthy for Sensitives
151-200	Moderately Polluted	55.5-150.4	Unhealthy
201-300	Heavily Polluted	150.5-250.4	Very Unhealthy
300+	Severely Polluted	250.5-500	Hazardous

History of the AQI.

[redacted]

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Lets start workg w/ a DQ [illegible]

$$\frac{\Delta n}{\Delta C} = .02n$$

or $\frac{dy}{dx} = k \cdot y$

$dy = k$

so $\frac{dy}{dx} = k \cdot y$

$\frac{dy}{y} = k\,dx$

$$\int \frac{1}{y}\,dy = \ln(y) + C = kx$$

$\ln(y) = kx - c$

$y = e^{kx - c_1}$

or $N = e^{k \cdot C} - e^{C_1}$

$N = e^{k \cdot C} + C_1$

Initial conditions $N = 100$ when $C = 10$ my
$N = 99.5$ when $C = 20$

$100 = e^{k \cdot 10} + C_1$

$99.5 = e^{k \cdot 20} + C_1$

or $.5 = e^{k \cdot 10} - e^{k \cdot 20}$

$.5 = e^{k \cdot 10 - k \cdot 20}$

$.5 = e^{k(10-20)}$

$.5 = e^{-10 \cdot k}$

$-.693 = -10 \cdot k$

$K = \frac{-.693}{-10} = .0693$

so $N \overset{?}{=} e^{.0693C}$

$N = 100e^{-.0693C}$

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You are on the right track but you have a little problem.

$\frac{\Delta n}{\Delta c} = \frac{P^{\%}}{100}\cdot N$ or $\frac{dN}{dc} = \frac{P^{\%}}{100}\cdot N$ or $\frac{dN}{N} = \frac{P}{100}\cdot dC$

for $x>0$ $\int \frac{dx}{x} = \ln(x) + C$ so $\ln(N) + C_1 = \frac{P}{100}\int dC$

or

$\ln(N) + C_1 = \left(\frac{P}{100}\right) C - C_1$ $3^{3-2} = 3^1 = 3 = 3^3 - 3^2 = 27-9$ NO

so

$\ln(N) = \left(\frac{P}{100}\right) C\, C_1$ or $N = e^{\frac{P}{10}\cdot c - C_1}$ $e^5\cdot e^3 = e^{5-3}$

$3^3\cdot 3^2 = \cdot$

$N = e^{\left(\frac{P}{10}\right)\cdot c}\cdot e^{-C_1}$ but $e^{-C_1} \neq C_1$ $10^3\cdot 10^2 = 10^{3+2}$

so $10^3\cdot 10^{-2} = 10^1$

$N = C_1 e^{\left(\frac{P}{10}\right)\cdot c}$ when $P=0, N=100$

$N = 100 e^{\left(\frac{P}{10}\right)\cdot c}$ when $c=10, N=99.5$

$99.5 = 100e^{x\cdot 10}$

$.995 = e^{x\cdot 10}$

$-5.012 = x\cdot 10$ $x = ;5012$

so $^{E-3}$

$N = 100e^{\cancel{-.5012\cdot c}\ -5.012E-4\cdot c}$ Ok. got it.

@ $x=10$, $N=99.5$

@ $x=50$, $N=97.525$

We do indeed have a daily mortality ~~[illegible]~~ of

0.2 - 0.6% Mortality

10 mg/m³

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We have, on a bad day: $\boxed{.05\%}$

$\frac{.4\%}{10\,\mu g/m^3}$ $\frac{2\%}{\text{Mortality}}$ $\boxed{.2}$

$\boxed{.01}$

We see now that we can use our series to approximate any function or its derivative, and then simply integrate it if need be.

It could well be that it has a closed integral solution as well.

$y' = g(y)$ are called autonomous diff equations

Feb 03 2016

It is on p69 of Diff Eq by Lomen that things finally start to get ~~interesting~~ .
"The epidemic model".
Prior to this, he is not really investigating DQs, he is investigating functions and working backwards.
But the epidemic model is truly a DQ examination, with no explicit solution to be had.

It brings up many interesting situations.

1. Modifying the DQ is much simpler than modifying a regression function. We have a max of 3 parameters to play with, whereas a regression equation could have 6-8 or more. This would be hopeless. So here is a case where working w/ a numerical solution of a DQ is easier than working w/ a regression equation.

2. He cannot come up w/ a good explicit equation or likely even a good regression equation.
I CAN!!
Therefore I have a distinct advantage. $\sum_{0}^{\infty} D^n = \sum_{n=1}^{\infty} a x^n$

Let's study this equation. It seems to have some similarities to the logistic equation.

3. The phase plane is an interesting topic.

Now let's get the death rate per year

per UN 2473018 in the most recent year.
This equates to 6775 per day.
per CDC
2,596,993 2013 =

Deaths per 100,000 = 821.5

$\frac{821.5}{100,000} = \frac{2596993}{x}$ x = 316,128,180 pop of US.

Published in Environmental Health Perspectives
Published June 2015

National Institute of Environmental Health Sciences.

$\frac{\text{2 day mortality}}{10\ \mu g} = 2\%$

Lets say we had 30 ug, then
$\frac{30}{10} \cdot 2 = 6\%$

Zero population
50-60 days/a year

~20 days out of year

Now for 50% we need $\frac{50}{6} = 8.3$ times

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Revisit the population decay problem:

$N = C_1 \cdot e^{\left(\frac{\overset{x}{\cancel{P}}}{100}\right) c}$

when $N = 100$, $C = 0$ so $100 = C_1$ so $N = 100 e^{\left(\frac{P}{100}\right) \cdot c}$

when $C = 10$, $N = \cancel{98}\ 102$ so

$102 = 100 e^{x \cdot 10}$

$\frac{102}{100} = e^{10x} \Rightarrow \ln(1.02) = 10 \cdot x \quad x = 1.98E\text{-}3$

so

$N = 100 e^{1.98E\text{-}3 \cdot c}$

			Linear
0	100		100
10	102.0		102
20	104.0		104
30	106.1		106
40	108.2		108
50	110.4	57	110
100	121.9		120
200	148.5		140
300	181.1		160
500	269.1		200
755	445.9		251

How many people are born each day in the US.
You could determine the breakeven point.

Birth rate 12.4 per 1000 population per year.
2013 Births per year 3,932,181

6 people born each
4 people die

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Many interesting questions come up here as to what it take to achieve zero pop growth.

Growth Rate: $\frac{3932181}{316128180} = +1.244\%$

Death Rate $\frac{2596993}{316128180} = 0.822\%$

$\Delta = 1.244 - 0.822 = +0.422\%$

To achieve ZPG, we need $3932181 - 2596993$
$\Delta = 1335188$ per year.

This means we need to increase the current mortality rate by
$\frac{1335188}{2596993} \doteq 51.4\%$

PM2.5
#1

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Date Location Wx, Conditions
Time Pop Visible Traffic PM2.5 T° Wind-Dr %RH Elev Vis
0900 01-28-16 0 Moderate 7 12°C 1-SE 23 1700 60
Location S.N.M Significant Aerosol Operation in Progress.
Traffic primarily over E-W Corridor. Some planes exercise
the bearing shift circa Gila Bend toward the SE.
Diffuse Cirro Stratus layer covers approx 50% of sky joined
with ~~of~~ multiple aerosol trails. Appears as a classic
aerosol operation. Haze not significant @ ground level @ this time.

Outskirts Tucson AZ Active Aerosol Operation, ~~Partly~~ Mostly Sunny, Diffuse Cirro Stratus
Pilot 01-28-16 2[illegible] ~~Moderate~~ Light ~~40~~ 45 28° 1-NE 2500 7% ~~55~~ 50
Gas 1315 Time This location is on edge of urban area.
Station.

01-28-16 1530 3 miles W of Colossal Cave, 20 miles E of Tucson. 50
Mostly Sunny, Large Scale banks of diffuse cirrostratus
Active aerosol operation today across Gila Bend-Tucson area.
1530 1 Light 35~~99~~ 28°C 1-W 5% 3300 50

01-28-16 ~~1630~~ Colossal Cave Tucson, Mostly Sunny, Significant Cirro-Stratus Banks
1630 0 Light 25 28°C 1-W 5% ~~3700~~ 3300 45

01-28-16 Collossal Cave Clear
2230 0 None 3 10°C 2-S 30% ~~3700~~ 3300 60

01-29-16 Colossal Cave NM Clear
0945 0 None 7 18°C 7-S 13% ~~3700~~ 3300' 60

01-29-16 Collosal Cave NM Approx 50% Diffuse CirroStratus
Partly Sunny. Significant Remaining Aer. Op. Impact.
1545 0 None 35 28°C 2-N 5% ~~3700~~ 3300 ~~60~~ 50

Date Location WX
Time Pop Vis. Traffic PM T° Wind-Dr %RH Elev Vis

01-29-16 Colossal Cave NM Clear
2045 0 None 1 8°C 0-NA 31% 3300 ~~3700~~ 60

01-30-16 Colossal Cave NM Mostly Sunny, altocumulus, Cirro-Stratus to E & S
1000 0 None 5 18°C 1-S 10% 3300 ~~3700~~ 60

01-30-16 Collosal Cave NM Mostly Sunny, Diffuse Cirro Stratus to W
1445 0 None 30 30°C 1-NW 5% 3300 ~~3700~~ 60

01-30-16 Collosal Cave NM Mostly Sunny, Diffuse Cirro-Stratus to W.
1730 0 None 8 23°C 1-S 11% 3300 60

01-30-16 Collosal Cave NM Clear, Night
2030 0 None 7 19°C 4-S 16% 3300 60

01-31-16 Colossal Cave NM Clear
0830 0 None 2 10°C 4-S 36% 3300 - 60

01-31-16 Colossal Cave NM Sunny, Some Cumulus Clouds
Significant weather, winds & rain forecast to approach tonight
1415 0 None 35 30°C 6-S 5% 3300 60

Increasing winds, Storm Forecast
01-31-16 Colossal Cave NM Mostly Sunny, Cumulo-Stratus
1815 0 None 12 21°C 12-W 13% 3300 60

02-01-16 Colossal Cave NM Partly Sunny, Cumulo-Stratus
~~Hea~~ Rain and strong wind storm last night.
0915 0 None 7 10 40% 3300 60

Health Index

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Light
Occ. Rain Showers
02-01-16 Tucson City, Trader Joes. Mostly Cloudy, Cumulo-Stratus
1230 3 None 15 18°C S-8 15% 2500 50

02-01-16 Collosal Cave NM Mostly Cldy, Cumulo Stratus
2045 0 None 1 8°C 4-N 31% 3300 60

02-02-16 Collosal Cave NM Clear, Occ. Small Cumulus Clouds
1030 0 None 0 6°C 5-N 30% 3300 ~~70~~ 90
Note: This is post rain storm.

02-02-16 Colossal Cave NM Clear
1800 0 None ~~0~~1 5°C 3-N 27% 3300 90

02-03-16 Colussal Cave NM Clear
0900 0 None 2 0°C 2-~~0~~S 38% 3300 ~~90~~ 80

02-03-16 Colossal Cave NM Clear, mild Haze developing @ ground level
1615 0 None 5 16°~~20~~ 2-SW 0% 3300 60

02-04-16 Colossal Cave NM Clear TA 13%
0845 0 None ~~2~~ 4 9°C 6-E 78% 3300 70

02-04-16 Clossal Cave NM. Mostly sunny. Light aerosol traffic. 2
Diffuse ~~Mild~~ Cirrostratus developing
2 1530 0 None Light 15 27°C 5-NW 5% 3300 65

0 02-04-16 Clossel Cave ~~NM~~, Clear
2245 0 None 2 2°C 0-NA 40% 3300 75

0 02-05-16 Colossal Cave NM, Clear, ~~Very~~ Slight Cirrus to W&S
1015 0 None 2 12°C N-2 16% 3300 70

Pop/sq. mi
0 <100
1 <1000
2 <10,000
3 <100,000
4 500,000+

Health Index

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0 02-05-16 Snyder Hill BLM Camp, SW Tucson, Clear
2300 1 None 2 12°C 0-NA 24% 2500' 70

SW of Tucson BLM
0 02-06-16 Snyder Hill, ~~SW Tucson~~ Mostly Sunny, Diffuse Cirrostratus to S
0915 1 None 6 20°C 8-S 5% 2500 60

BLM SW of Tucson
0 02-07-16 Snyder Hill Mostly Sunny, Haze & CirroStratus to S.
0930 1 None 2 21°C 5-S 5% 2500 45-S 60-E,W,N
Haze bank to south with slightly diminished visibility
All other quadrants primarily clear. No traffic.

Edge Mostly Sunny
2 02-07-16 Tucson ~~Outskirts~~ (S) Increasing Haze, Diffuse Cirrostratus
1030 2 None ~~14~~20 22°C 5-S 3% 2500 45-S 55-E,W,N
Haze bank to S. gradually diffusing toward other
quadrants & descending to lower elevations, mildly
diminished visibility to S. Traffic on Highway distant 100'.

BLM
2 02-08-16 Snyder Hill Mostly Sunny, Diffuse CirroStratus bank
to S. (Nogales - US Border region)
0900 1 None 20 24°C 4-SE 3% 2500 45-S 60-E,W,N

4 02-09-16 BLM Snyder Hill, Sunny w/ Diffused Haze to Ground Level
on all quadrants
1030 1 None 35 26°C 6-S 3% 2500' 45 all quadrants

02-09-16 BLM Snyder Hill Clear w/ Mild Haze @ Ground Level
3 1530 1 None 23 28°C 4-NE 3% 2500 50

02-09-16 BLM Snyder Hill Clear
2 1815 1 None 13 25°C 3-NE 5% 2500 55

0 02-09-16 BLM Snyder Hill Clear
2130 1 None 6 13°C 0-NA 22% 2500 65

[redacted]

3 02-10-06 Clear w/ ~~minor~~ moderate haze to south. BLM Snyder Hill
0930 1 None 25 26°C 5-SE 4% 2500 50-S, N 60-W, E

02-10-06 Desert Museum, W. Tucson, Clear, Moderate Evenly Distributed Haze
1330 1 None 33 30°C 5-SE 2% 2800' 55

a 02-10-06 Snyder Hill BLM, Clear
0130 1 None 9 15°C 0-NA 21% 2500 60

2330?. ~~233~~ 02-10-16 Snyder Hill BLM Clear
2130. 1 None 6 15°C 0-NA 21% 2500 65

02-11-16 Snyder Hill BLM Clear, Mild Haze Distributed
0800 1 None 2 15°C 1-SE 21% 2500 65

Move Today 02-11-16 Cochise Stronghold az Remote location. Clear, Mild Haze Across Vistas, Camp in Shade
1 1600 0 None 10 22°C 0-NA 10% 5000 Limited View Estimate 65
No fires in Camp: See Campfire Non Outdoor 02-11-16

02-11-16 Cochise Stronghold, Clear, Box Canyon Site, Star Estimate
2345 0 None 1 12°C 0-NA 23% 5000' ~~60~~ 65

~~02-12-16 Apache Fly Ash Operations, near Pearce Az~~ Pearce
~~approx 8 miles N. of Pearce, Clear, Modest Haze~~
~~across region. Not distinctive to Fly Ash~~
~~1515 0 None~~
02-12-16 Pearce az edge, ~~Clear,~~ Mostly Sunny, Diffuse Cirro Stratus bank to SW. Mild Haze @ Ground Level All quadrants
1530 0 None ~~45~~ 50 34°C 1-SE 2% 5000' 55
See Fly ash Msmt @ identical level 8 miles
Fly Ash Plant appears perfectly clean.

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Objection to AQI therefore are:

1. The AQI scale is heavily biased toward extreme concentration levels that far exceed the practical range of health impacts which are known to occur @ ~~suprising levels~~ @ suprisingly low concentration levels.

2. The scale is dramatically underweighted in the range where it will have the greatest practical benefit, i.e. low to moderate concentrations

3. The information presented via the portals does not reflect the dynamics of air pollution as they are measured and observed to occur.

The requirements for change are therefore

1. Adopt a scale which ~~recognize~~ and ~~ack~~ acknowledge and emphasize the concentration levels that are most likely to occur and that are known to affect human health and mortality @ significant levels.

2. Weight the presentation of the ~~data~~ PM 2.5 concentration in an even manner across the lower concentration levels that are known to impact human health and mortality, and

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Correspondingly, Change the Color Coding to reflect this [illegible] [illegible] less weighting.

as it now exists

3. Discard the AQI and report [illegible] PM [illegible]. Concentrations directly without a mapping and process in the data presentation

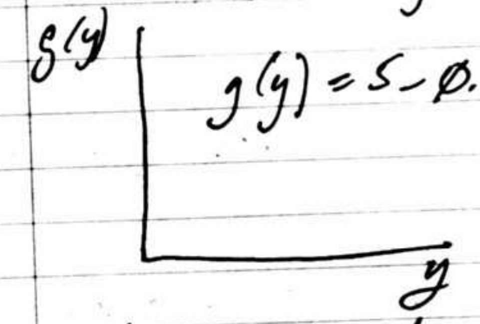
4. The web portal must incorporate real time & short term Concentrations in a dynamic fashion including max value achieved as opposed to averaging value over a time period that negates the impacts of short term exposure.

Feb 04 2016
Returning to the DQ

$y' = 5 - 0.5y - 5e^{-y}$

There are many interesting things to this equation.
First, you can see by plotting slope graphs that
$y' = 5 - 0.5y - 5e^{-y}$
IS TOTALLY DIFFERENT
and it has nothing to do with
$y' = 5 - 0.5x - 5e^{-x}$
They result in two totally different solutions
The solutions have nothing to do with one another.

But also on p69 Loman actually does draw
essentially
$f(x) = 5 - 0.5x - 5e^{-x}$
but what he really draws is:

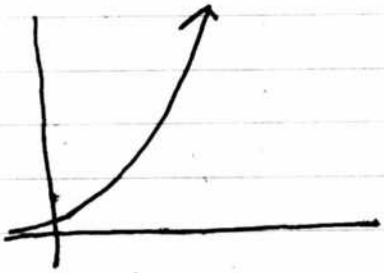


Which is like drawing $y' = f(x)$
but apparently it really is not and
he learns some important ~~quantitative~~
qualitative info by doing so.
So there is a lot of food for thought here
w/ this equation.

So lets play around with this some.
What does } $y' = 2x$ mean vs $y' = 2y$???

$\frac{\Delta y}{\Delta x} = 2 \cdot x$ $\qquad$ $\frac{\Delta y}{\Delta x} = 2y$

$\Delta y = 2 \cdot x \cdot \Delta x$ $\qquad$ $\Delta y = 2 \cdot y \cdot \Delta x$



The slope fields are entirely different from one another.

$\frac{\Delta \text{ in Population}}{\Delta \text{ Concentration}} = K \cdot \text{Concentration}$ $\qquad$ $\frac{\Delta \text{ Population}}{\Delta \text{ Concentration}} = K \cdot \text{Population}$

So in both case you have a population that is dependent upon concentration of a pollutant.

In the first case, a "shift" is a function of the pollutant and not the population.

In the second case, a "shift" is a function of the population itself and the change in concentration can be regarded as a constant.

Think about this, and how fundamentally different the interpretation is.

Which now naturally leads to the evolution of the possibility that a "shift"

is a function of <u>both</u> the concentration AND the population as well.

This is quite feasible and is therefore the basis for a PARTIAL DIFFERENTIAL EQUATION

ie

$$\frac{\partial U}{\partial x \partial y} = \frac{\partial U}{\partial x} + \frac{\partial U}{\partial y}$$

$$\frac{dz}{dt} = \frac{\partial z}{\partial x}\frac{dx}{dt} + \frac{\partial z}{\partial y}\frac{dy}{dt}$$

So what does a partial diff eq look like?
They look like this:

$U(x_1, x_2)$ $\frac{\partial U}{\partial x_1} - \frac{\partial U}{\partial x_2} = 0$ is a 1st order PDE

$U(x_1, x_2, x_3)$ $\frac{\partial^2 U}{\partial x_1^2} + \frac{\partial^2 U}{\partial x_2^2} + \frac{\partial^2 U}{\partial x_3^2} = 0$ is a 2nd order PDE

Casio can solve for the zeros of the diff eq.

Feb 05 2016

1. Images need to be enlarged.
2. Let's assume 2% Short Term & 7% Long Term Mortality Increase per 10ug/m3.

Let's try to put this into perspective.

We now have 2596993 deaths per year - 2013
This equates to: = 7115 per day.
We should find the data for 2003, for example, births, deaths & population.

.02(7115) = 142 people per day.

Increase in PM2.5	US Increased Mortality
0 (.02) = 0%	0
10 (.02) = 2%	142
30 (.02) = 6%	427
50 (.02) = 10%	712

Now, this is for short term exposure, which is only 1 day.
Let's assume 30 ug.
Assume 10% of days show pollution

Now obviously we have a situation between ST & LT exposure.

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ST exposure 2 days = 2%

LT exposure 365 days = 7%

so assume a logarithmic function.

$$\text{Mortality}\,\% \cong 1.33 + 0.96\ln[(\text{days exposure})]$$

$$r^2 = 1$$

Now assume 10% of year polluted @ 30ug

$$\text{Mortality}_{10}\,\% = 1.33 + 0.96\ln[(36.5\,\text{days})] = 4.78\%$$

$$4.78\left(\frac{30}{10}\right) = 14\%$$

What if it were linear?

$$\text{Mortality}_{10}\,\% = .014(\text{days}) + 1.97$$

$$= .014(36.5) + 1.97 = 2.48 \cong 2.5\%$$

7115 people per day

Now 30ug $\Rightarrow \frac{30}{10}(2.5\%) = 7.5\%$ Increase in Mortality

Days @ 10% Pollution PM2.5 Increase	Deaths (2.5%) Linear (7.5	Deaths (4.8%) Logarithmic	$\bar{X}$
0	0	0	0
10	178	342	260
20	356	683	520
30	534	1025	780
50	889	1708	1299

This looks very realistic. 30ug 10% of days conservatively leads to an estimate of 780 additional deaths per day.

$\frac{780}{7115}$ = 11.0% increase in mortality

Eq. to Strokes, Alzheimers & Diabetes combined

The model proposed is

$$y = ax+b \frac{+c}{2} + d\cdot\ln(x)$$

$$y = \frac{1}{2}\left(b+c+ax+d\cdot\ln(x)\right) = C_1 + C_2X + C_3\ln(x)$$

Our two models are $M_{\text{linear}_{10}} = 0.014(\text{days}) + 1.97$

$$M_{\ln_{10}} = 0.96\ln(\text{days}) + 1.33$$

$$\text{Average} = \frac{1}{2}\left(3.3 + (.014\cdot\text{days}) + (0.96\ln(\text{days}))\right)$$
$$= .007(\text{days}) + 0.48\ln(\text{days}) + 1.65$$

*

let days = 2 Avg = 2.0%] very good.
days = 365 Avg = 7.0%]
days = 30 Avg = 3.5% This seems quite realistic.

PM2.5	M%
0	0
10	3.5%
20	7.0%
30	10.5%
50	14%

.105(7115) = 747 people per day
= 272,682 per year

or .105(2596993) = 272684 per year OK

Mistake If we lose 272684 die per year, what does this equate to :

5 ~~4th~~ Stroke 128978
6 ~~5th~~ Alz: 84767
7 6th Diab. 75578
$\Sigma = 289323$ within 6% of this.

5 ~~4th~~ Stroke 128978
6 ~~5th~~ Alz 84767
8 ~~7th~~ Infl. & Pneumonia 56979
Σ 270724 This works
$\Delta = 0.7\%$ vs 272684 from 30y 36.5 days
Very sad.

1 ~~Cancer~~ Heart Disease 611,105
2 Cancer 584,881
3 COPD 149,205
4 Accidents 130,557

Feb 08 2016

We are back to our diff eq. We are seeking a case where the DQ evolve from collected data. We do not have that yet but we are working on it.

$x'' + 3x' + 2x = 0$

is a linear autonomous diff eq.

The solution is $x(t) = C_1 e^{t} + C_2 e^{-2t}$

$x = -1 \quad x = -2$ $\qquad D^2 + D$

$x_q = C_1 e^{-t} + C_2 e^{-2t}$ $\qquad y'' + y' = 0$

$D^2 + D = 0 \qquad x = -1, 0$

$D^3 + D^2 + D = 0 \qquad x = 0,$

$D^2(D+1) = 0 \qquad x = -1, \pm i$

$D^4 + D^3 + D^2 + D = 0$

$D(D^3 + D^2 + D + 1) = 0 \qquad x = 0$ only one real root.

$1 \qquad x = 0, \ -1?, \ i, -i?$

Math Studio method:

DSolve$(y''(x) + 2y'(x) + y(x) = x, y(x), no)$

DSolve$(y''(x)_+_2y'(x)_+_y(x)_=_x,_y(x),_no)$

Single quotation character is used at all times to indicate the derivative

$D^2 + D = 0 \Rightarrow C_1 e^{-x} + C_2$ OK

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$D^3 + D^2 + D = 0$

$C_1 \cos\left(\frac{\sqrt{3}}{2} x\right) e^{\frac{-x}{2}} - C_2 \cos\left(\frac{\sqrt{3}}{2} x\right) e$

$D^4 + D^3 + D^2 + D = 0$

0, -1, i, -i yields $C_1 \cos x - C_2 e^{-x} - C_3 e^{-x} + C_4 \sin(x) + C_5$

We have it. It must be an even number of terms.

yes $= C_1 + C_2 \cos x + C_3 \sin(x) + C_4 e^{-x}$ excellent.

but actually it is (NO –

~~$C_1 \cos(ax) e^{bx}$.~~

$D^6 + D^5 + D^4 + D^3 + D^2 + D = 0$

$y = C_1 \cos bx e^{ax} - C_2 \cos bx e^{ax} - C_3 \cos bx e^{ax}$

$- C_4 \cos bx e^{-ax} - C_5 \cos bx e^{-ax}$

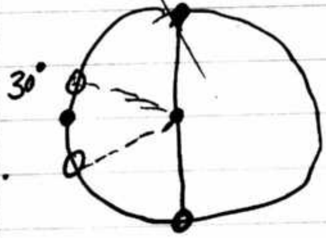
$b = \frac{\sqrt{3}}{2}$ $a = \frac{1}{2}$

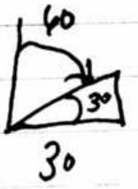
$= 30°$ $= 60°$

$y = C_1 + C_2 e^{-x} + C_3 \cos x + C_4 \sin(x) + C_5 (\cos bx) e^{ax}$

$+ C_6 \sin(bx) e^{ax}$

$b = \frac{\sqrt{3}}{2}$ $a = .5$





$\cos 30° =$

$\sin 60° =$

$\frac{\sqrt{3}}{2} = .866$ $\sin 60 = .866$

Recovery again of Exponential Harmonics.

$y^6+y^5+y^4+y^3+y^2+y'=0$

n $D^6+D^5+D^4+D^3+D^2+D=0$

$b=\sin\left(\frac{360}{6}\right) \qquad a=\overset{\cos}{\cancel{\sin}}\left(\frac{360}{6}\right)$

$=.866 \qquad .5$

$b=\sin\frac{2\pi}{n} \qquad a=\cos\left(\frac{2\pi}{n}\right)$

n = order of the even differential equation

So I have it again!

Series must be even terms, ie. D^n $n=$ even

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[redacted] Feb 09 2016

Back to Diff eq

Many interesting topics and we have already just started. We have a DQ that we have no idea how it evolved. We have the understanding now of autonomous vs non-autonomous diff eq and how important the distinction is. You never did understand this before and Lorenz is the one that pointed it out.

[redacted]

Also, you "linear DQS w/ constant coefficients" you now realize is an autonomous diff eq form

eg

$$y''(x) + y'(x) + y(x) = 0$$

$$D^2 + D + ? = 0$$

So you know that

$$y''(x) + y'(x) = 0$$

$$\Rightarrow D^2 + D = 0.$$ This is certainly a good example.

Lorenz does not seem to separate out this topic like you are used to but what he has done instead is to distinguish between autonomous and non-autonomous diff eqs.

P 498

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An autonomous form is

$x'' + 3x' + 2x = 0$

Solution is
$x(t) = C_1 e^{-t} + C_2 e^{-2t}$

A non autonomous form is

$x'' + 2tx' + (1 + t^2)x = 0$

Solution is
$x(t) = 10e^{-1/2} \cdot e^{-\frac{1}{2}t}$

So from the solution you cannot tell if an equation was autonomous or not.

So what is the definition of autonomous vs non autonomous.

Autonomous $\frac{dy}{dx} = g(y)$

Examples:

$y' = ky$ exponential
$y' = ay(b-y)$ logistic
$y' = y^2$
$y' = (y-1)^{2/3}$
$y' = 5 - 0.5y - 5e^{-y}$

y is always really $y(x)$

Nonautonomous $y' = g(x,y)$

Autonomous equation says a change in a function is somehow a a·d·[illegible] function or operation upon the original function.

So autonomous means exactly that.

A change in a function is some operation on the existing or original function. That is a headful to ~~stor~~ think about, no doubt.

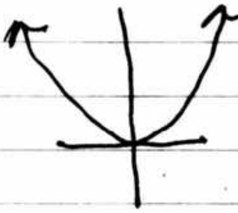
A non-autonomous diff eq is where a change in a function is an operation upon an independent variable as well. This seems to be generally a simpler case?

So this distinction between an autonomous or a non autonomous equation was a really really important distinction to make.
I do not think you were really even aware of the situation before.

$\frac{dy}{dx} = kx$	or $\frac{dy}{dx} = ky$
Non-Autonomous.	Autonomous
Change w.r.t. an independent variable.	Change wrt an operation on the original function.
Seems simpler.	A most interesting "circular" situation.

Let's graph these to see the difference.

The solution here is parabolic.



x=0, y=0
is not in the domain.
This is because the
solution involves
a ln function.

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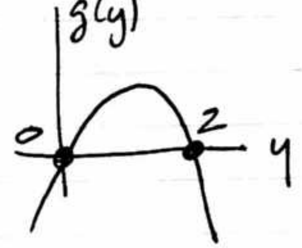
So already the solutions are entirely different and I do not think that there really is even any basis for comparison because we understand that the operator is really entirely different in each case.
I do not think that I would even try to compare them.

So before we can even take on "Phase Line Analysis" we need to understand "equilibrium solutions"!
p66 makes a reference to this - Lomen
Lets find the original.)

You find equilibrium points by graphing the solution of an autonomous diff eq as it is set to zero.
It must satisfy the uniqueness theorem before we do so.

(Also note, the derivative of the logistic equation is a specific quadratic form.

When we look @ equilibrium points we are actually looking @ a graph of the form



as in $y' = y(2-y)$
or we are plotting
$y(2-y) = 0$.

We can see how this applies to an autonomous equation. I wonder if it can apply to non-autonomous equations?

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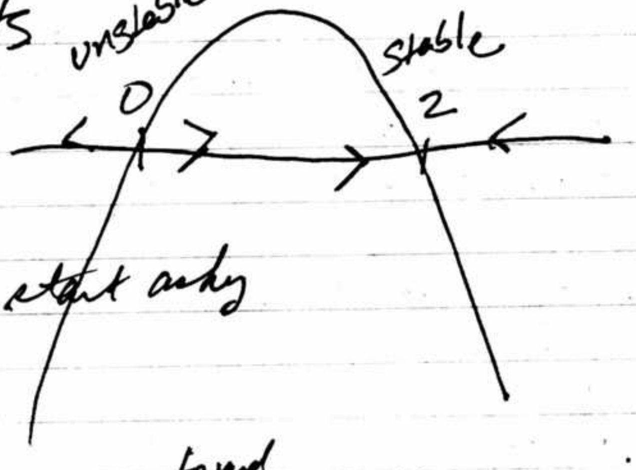
So in the case 0 & 2 are the equilibrium points



so we start asking

Arrows pointing toward an equilibrium point indicate a stable equilibrium point.
Arrows pointing away from an equilibrium point indicate an unstable equilibrium point.

Next questions:

see p 67. 1. How do you know which way to draw the arrows?
2. What is a stable equilibrium point?
3. What is an unstable equilibrium point?

These questions still exist.

By plotting a solution w/ initial condition we can start to see what it means to have a "stable equilibrium point".
There's a logistic equation and it approaches 2

There is no solution when $x=0$, $y=0$ so $y=0$ is an unstable equilibrium point.

OK, this is better.

Ok, so how you begin to evaluate a diff eq you can

1. Ask, is it autonomous or not, think about what this means.
2. Plot the slope field & investigate some initial conditions
3. Determine the equilibrium points & stability of these points.

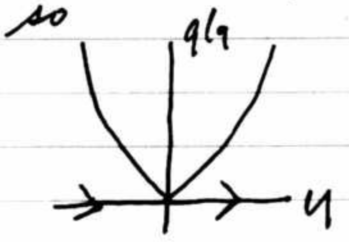
These three things provide a qualitative view of autonomous diff eq. & thus is very worthwhile.

So Consider

$y' = y^2$

1. It is autonomous? yes
2. What are the equilibrium points? $y^2 = 0$ only $y = 0$

so



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Now we may be in better position to examine the introduced equation:

$$y' = 5 - 0.5y - 5e^{-y} \quad \text{see?} \left\{ \begin{array}{l} \text{a constant} \\ \text{a linear term} \\ \text{an exponential term} \end{array} \right.$$

1. First, it is autonomous, that alone says something of importance. $\frac{\Delta}{\Delta x}$ = operator on $y(x)$

2. Next a slope graph is insightful.
This has a strong similarity to the logistic equation
There is certainly an Equilibrium point
3. in this graph.

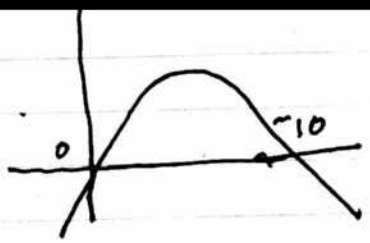
3. Now lets investigate equilibrium pts:

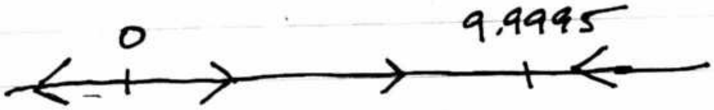
Set $y' = 0$ and find the roots

$$5 - 0.5y - 5e^{-y} = 0$$

One root is @ zero. lets plot also.
The next root is near 10.
How do we know how many roots there are?
Next we solve to find out if it is 10 or not...
It is not 10. It is 9.9995
How about that? This means do not assume!

[redacted]





So now we can see that 0 is an unstable (divergent) point and 9.9995 is a stable point (convergent) because

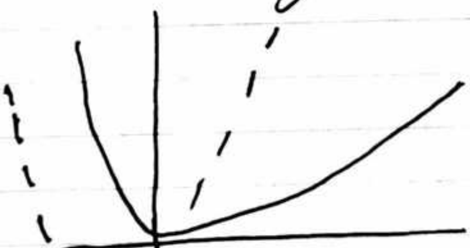
arrows pointing in : stable (convergent)
arrows pointing out : Unstable (divergent)
arrows right or arrows left : semi-stable

This is really quite marvelous, isn't it. You know quite a lot about the solution before any specific solution is determined. You know its shape & stability across the various domains. Can this work w/ non-autonomous solutions also?

Next we look @
$y' = x - y$ p82 Lomen

Solution has the form

Now Lomen is going to show us how to analyze this graphically.



Aerosol op Profile

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12/25 (#12)
12 0745 2
1130 25
1530 10
1600 5
1630 20

1/12
33 1230 20

Ops 1/16 ~~2~~
0 36 0915 ~~20~~ 2
1 1115 ~~11~~ 20
2 1500 ~~3~~ 11
3 1930 ~~2~~ 3

Ops 01/19
4 42 0915 2
5 1100 8
6 1245 15
7 1415 40
8 1445 45
9 1515 52
10 1525 57
11 1630 36
12 1730 5
13 1800 2
14 1900 2

01/20/16
54 0845 2 15
Postops 1130 6 16
1215 20 17
1400 20 18
1700 23 19
1745 3 20

01/21/16
60 0930 2 21
ops 1115 32 22
1530 12 23
1730 2 24

Ops 01/23/16
70 0900 2 25
1245 40 26
1445 25 27

Ops 01/28/16
86 0900 7 28
1315 45 29
1530 35 30
1630 25 31
2230 3 32

Postops 01/29/16
91 0945 7 33
1545 35 34
2045 1 35

Profile at Aerosol of
Need Exponential Harmonics.

Stats on PM2.5
$\bar{X} = 17.4$
$\sigma_s = 16.3$
max = 57

01/30/16

94	1000	5	36
Postop	1445	30	37
	1730	8	38
	2030	7	39

0131/16

98	0830	2	40
	1415	35	41
	1815	12	42

Max occurs @ ~ 1430. Value = 32

Approx values will be

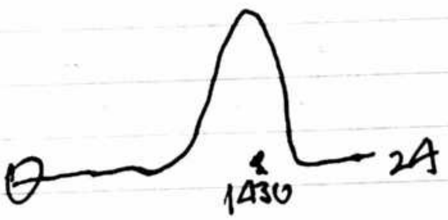
$\bar{X} = 20$

$\bar{X} = 10$

Time	Value	
9	2	1
10	8	2
11	16	3
12	24	4
13	30	5
14	33	6
15	32	7
16	28	8
17	20	9
18	11	10
19	2	43
20	2	44
21	2	45
22	2	46
23	2	47
24	2	48

n = 51

1	2
2	2
3	2
4	2
5	2
6	2
7	2
8	2



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Aerosol op Profile

Another way to do this is to only plot what is daylight hours ie 0900 - 1800

A Quartic function works fairly well between 0900 and 1900. (10 hrs) These are reasonable.

HR	Quartic Value (PM 2.5 Count)
8.5	1
9	2
10	8
11	16
12	24
13	30
14	33
15	32
16	28
17	21
18	11
19	2

Ok, this section of a quartic gives a good cubic

$PM2.5 \simeq -1.12\,hr^2 + 31.51\,hr - 190.7$

$r^2 = 0.95$ Mse $= 9.26$

Aerosol Op Profile

Next, we can integrate the cubic from 8.5 to 19.

= 214.025 HR·PM2.5 Count

Mean Value = $\frac{214.025}{19-8.5} = \underline{\underline{20.4}}$

But if we take the same integral and find the mean value of 24hrs we get

$$\frac{214.025}{24} = 8.9$$

$\frac{20.4-8.9}{20.4} =$ $\underline{\underline{56}}$ % reduction

Now including night Contributions

$214.025 + 2(24-(19-8.5))$

$= \frac{241.0}{24} = \underline{\underline{10.0}}$

1. Sunlight
2. Maximums
3. Average.
4. Quick vs Slow Poison

$\frac{20.4-10.0}{24} =$ 43.3% reduction

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Feb 12 2016

We continue w/ our Diff Eq

$y' = x - y$

We know what the slope field looks like by plotting it. Also some various solutions can be investigated. What else?

But before we do this, what about the average of a function? eg $y = x^2$

x	y
0	0
1	1
2	4
3	9
4	16
5	25
6	36

$\bar{x} = 13$

$$\int_0^6 f(x) = 72$$

$$\frac{72}{6-0} = \underline{12}$$

x	y
7	49
8	64
9	81
10	100

$x = \frac{385}{11} = 35$

$$\int_0^{10} f(x) = \frac{333.3}{10} = 33.3$$

There is indeed a "mean value theorem" of integral calculus. P255 Schaum Calculus.

I think that this is right

$$\bar{f}(x) = \frac{\int_a^b fx}{b - a}$$

but you need to find this.

The mean value theorem is

$$\int_a^b f(x)\,dx = (b-a)\cdot f(x_0)$$

So the question is, what is $f(x_0)$?

I think that it is the mean value of the function over the interval, but how do you prove this?

Ok, we have found it! P261 Schaum

It is called the "average ordinate", exactly what I was looking for.

$$\text{Average Ordinate of } f(x) = \frac{\int_a^b f(x)\,dx}{b-a}$$

Perfect. Indeed it is.
~~It~~ also called the average value.
In our case, the average PM 2.5 count w.r.t. time

Lets go back to our PM problem.

So we do have the average value of the quadratic estimation.

Now, what is interesting here is that we have an average of 20.4 for $(19-8.5)$ hrs! = This is 10.5 hrs!
The remaining time w/in the day is 24 - 10.5 = 13.5 hrs

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The true folly of Averaging.

Assume we have a spike every day for
100 PM 2.5 for 1 hr. and 10 for remainder

Our average is therefore $\frac{23(\overset{10}{\cancel{14}}) + 1(100)}{24} = \underline{\underline{14}}$

Would you not like to know
that you had been affected by a 100 PM spike?

Let's go 5 for 23 hrs.

$\frac{23(5) + 1(100)}{24} = 9$ This is a good example

Use this as an extreme example.

What if that happened every day of the year?

$= 365\frac{(100)}{1hr} = 36500$ PM2.5·1hr.

$= \frac{36500}{24 hrs} =$ 1520.8 exposure ~~per day~~.

Total Average Count Per Day $\bar{9}$ PM 2.5 (365 days) = 3285 PM2.5 Total Exposure.

23(5) + 1(100) = 215 per day (365 days) = 78475

$\frac{78475}{3285} = \underline{\underline{23.9}}$ times as much particulate matter in a year.

An average is problematic
w/ pulsed or spiked data.

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A simpler, more realistic example.

19 hrs @ 5 + 5hrs @ 20.

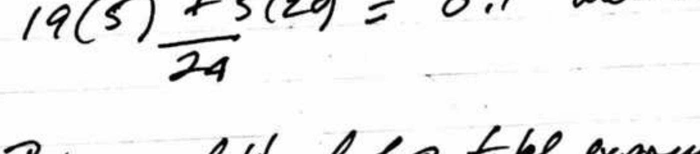
$\frac{19(5) + 5(20)}{24} = 8.1$ well within limit of EPA.

But now let's look @ total exposure to PM2.5
as expressed by $\sum$ PM2.5 · time

In first case we have assumed $\overset{\text{per hr}}{(8.1)}$ (24hrs) (365days)
= 70956
PM2.5

2. In second case we have
~~thus~~ 19(5) + 5(20) = 195 per day. = 71,175 PM so this
is the same.

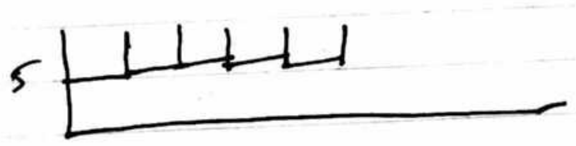
Scenario A



= 3285

Which would you
rather be subjected
to and why?

Scenario B



How do you
quantify this?

$\cancel{\left(\frac{23}{24}(5) + \frac{1}{24}(100)\right)} \cdot 365 =$

365(100 − 5) = 34765 additional exposure.

$\frac{34765}{3285}$ = 10.6 times the exposure as the first
case.

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So the issue here is average exposure vs total exposure.

Avg ~~Exposure~~ $=(f_1 \cdot H)$

Total ~~Avg~~ Exposure Per Year $= \left(\frac{t_1 \cdot L + t_2 \cdot H}{t_1 + t_2} \right) \cdot 365 \cdot 24$

Based upon Avg

$= \cancel{t_1 / 24}$

Total Exposure Per Year $= \cancel{Q} \left(t_1 \cdot L + t_2 \cdot H \right) \cdot 365$

Lets form this ratio:

$$\frac{(t_1 \cdot L + t_2 \cdot H) \cdot 365}{1} \quad \frac{(t_1 + t_2)}{365 \cdot (t_1 L + t_2 H) \cdot 24}$$

⇒ So total exposure is the same

The issue is max Exposure, not total exposure.

In Case A you have measured exposure 365 days of "safe levels".

In Case B you have ~ $\frac{100}{5}$

or 20 times max exposure $\frac{365 \text{ hrs})}{365 \text{ days} (24 \text{ hrs}} =$

.042 of year
or 15.2 days.

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This work with the average ties in with your mortality model.

From our previous formula we have:

$$\text{Mortality}_{10}\% = .014(\text{days}) + 1.97$$

$$= .014(15.2 \text{ days}) + 1.97 = 2.2\%$$

but we have

$$\frac{100}{9} = 11.1 \text{ times the "average exposure"}$$

This leads to an expected increase in mortality of

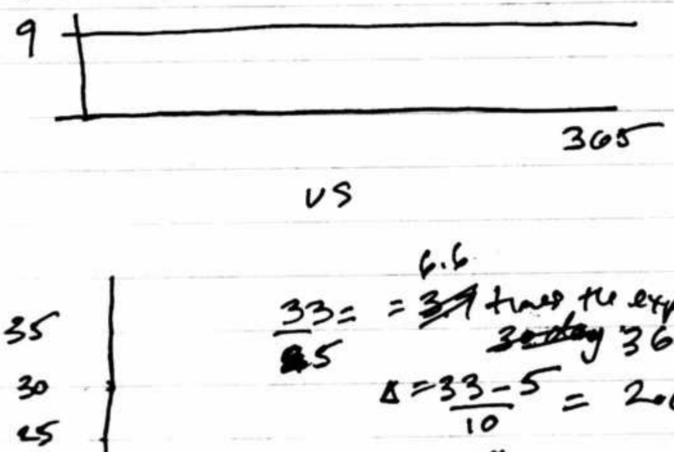
$$11.1(2.2\%) \cong \underline{\underline{24\%}}$$

So now you see how significant this is.

OK, you are starting to get there.

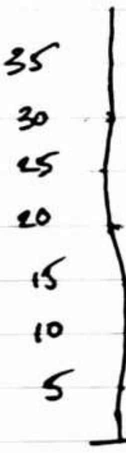
This is why real time exposure data is important.

Now look @



vs

max of 33
30days
per year



$\frac{33}{5} = = \cancel{3.7}\overset{6.6}{} \text{ times the exposure}$

~~30 day~~ 36.5 days per year

$$\Delta = \frac{33-5}{10} = 2.8 \text{ sets of } 10\mu g/m^3$$

$$\text{Mortality}_{10}\% = .014(36.5) + 1.97 = 2.5\%$$

$$(2.5\%)(2.8 \text{ sets of } 10) = 7\% \text{ increase in mortality.}$$

and yet you would never know it by the average.

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No Campfires 02-12-16 Cochise Stronghold, Partly Sunny, Diffuse Cirro Stratus Overhead
1600 Ø None 30 28°C 1-SE 3% 5000 Est 55

No Campfires 02-13-16 Cochise Stronghold Clear
0845 Ø None 2 14°C 0-NA 23% 5000 60

No Campfires 02-14-16 Cochise Stronghold Clear
1500 Ø None 18 26°C 3-SE 3% 5000 55

02-14-16 Cochise Stronghold Mostly Clear but Haze around 1/4 Moon Moon
2215 Ø None ~~Light~~? 0 17°C 1-SW ~~0-NA~~ 7% 500 5550
Interesting observation tonight. Haze building around 1/4 Moon. Sunlight activates materials. Does moonlight also activate? Slight elevated night count. Unusually warm air. Definitely increased haze to south visible by moonlight.
Unusually ~~Exceptionally~~ warm air tonight.

02-15-16 Cochise Stronghold, AZ Clear
0145 Ø None 4 16°C 1-SW 11% 5000 60

02-15-16 Cochise Stronghold Clear
0930 Ø None 7 18°C 1-SE 15% 5000 60

02-15-16 Cochise Stronghold, Clear
1430 Ø None 8 23°C 2-SE 5% 5000 60

02-15-16 Cochise Stronghold Clear
2130 Ø None 2 11°C 0-NA 30% 5000 60

02-16-16 Cochise Stronghold, Clear
0900 Ø None 4 14°C 1-SE 30% 5000 65

PM 2.5 #8

Page 318 heighth

02-17-16 Cochise Stronghold, Clear, Moon 3/4
0000 0 None 5 16°C 0-NA 20% 5000 65

02-17-16 Cochise Stronghold Clear
1015 0 None 7 18°C 1-SE 18% 5000 65

02-17-16 Cochise Stronghold Clear
1645 0 None 6 22°C 1-SE 11% 5000' 65

02-17-16 Cochise Stronghold, Clear
2300 0 None 4 21°C 4-SE 6% 5000' 65

02-18-16 ~~Alamo~~ Cochise Stronghold AZ, Clear
1100 0 None 4 22°C 4~~[illegible]~~-SE 12% 5000' 70

02-18-16 Cochise Stronghold Cloudy, Stratus
1930 0 ~~Not Visible~~ ~~Not Visible~~ NO VIEW 1 22°C 6-~~SE~~ 12% 5000' 70
Note: Clouds moved in from W. this afternoon.
Note: Skies clear later by 2245 - no traffic visible

02-19-16 Cochise Stronghold, Mostly Cldy, Diffuse ~~Cumulus~~ Cumulo-Stratus
0915 0 None 10 17°C 1-SE 33% 5000 60
Haze layer ~~be~~ overhead mixed w/ cloud forms.

02-19-16 Cochise Stronghold, ~~Mostly Sunny~~ Partly Cldy, Diffuse Cumulus, Haze visible overhead throughout
1345 0 None 30~~[illegible]~~ 29°C 1-S 3% 5000 ~~55~~ 50 50 and
Stronger haze visible to ~~N~~ from Pearce AZ. Strong haze visible to S. towards sun.

02-20-16 Cochise Stronghold, High Haze Overhead, Ring around Moon
0030 0 None 2 13°C 0-NA 21% 5000 60

to all quadrants.
Partly Sunny Extensive Haze
02-20-16 Cochise, ~~Clear~~, Diminished Visibility
0345 0 ~~None~~ Light 4 13°C 0-NA 34% 5000 ~~60 60~~ 55

Heavy
02-20-16 Cochise Stronghold Haze to all quadrants
1000 0 Light 22 17° 1-NE 16% 5000 50

Active Operation
Eastern outskirts of
02-20-16 Tombstone, Extreme Haze to South towards Mexico
Moderate Haze to all quadrants.
1100 0 Light 25 26°C 1-SE 4% ~3000'? 50

Active Operation
02-20-16 Tombstone Significant Haze to All Quadrants.
Active Operation Aerosol, Diffuse Cirro Stratus
1630 1 Moderate 40 30°C 4-NW 3% 3000? 50

Full Cover
02-20-16 Cochise Stronghold Diffuse Cirro Stratus
1930 0 Not Visible 7 16°C 1-SE 23% 5000 50

02-21-16 Cochise Stronghold, Clear
1345 0 None 20 26°C 2-E 8% 5000' 60

02-21-16 Cochise Stronghold, Clear
1615 0 None 14 23°C 2-NW 7% 5000 60

02-22-16 Cochise Stronghold, Clear
0015 0 None 7 16°C 3-E 19% 5000 60

02-22-16 Cochise, Clear
0900 0 None 6 16°C 2-SE 13% 5000 60

02-22-16 Cochise, Clear
1530 0 None 2 22°C 8-SE 5% 5000 60
Note: Especially clear air for midday hours of late.
Increased winds; cold front is forecast.

PM 2.5 #8
Page 2

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02-23-16 Cochise Clear
1030 0 None 3 15°C 3-SE 9% 5000 65
Rapid Transformation from Clear to Diffuse Cirrostratus Layer

02-23-16 Cochise. Massive Night Aerosol Operation.
Commences @ approx 2100. Sky transformed
from Clear to massive network of NW-SE oriented
trails visible under a full moon (+1 day).
False / Anticipate increased PM count during sunlight hours
tomorrow. No visible PM effect @ night materials fresh
or without time allowance for descent. overhead, not @ ground level.
2230 0 Heavy 2 10°C 0-NA 20% 5000 ~~60~~ 65

Full Moon period

~~0800 Cochise, Clear~~

02-24-16 Cochise, "Clear" 42% 65
0800 0 None 2 3°C ~~4°C~~ 0-NA ~~40%~~ 5000 ~~60~~
No Sign of ~~Arg~~ previous night operation visible
Cold Front in progress.
Higher humidity, lower temperatures.
Sun rising now over camp area.
Refer to earlier prediction paper related to humidity.

~~1015~~ 02-24-16 Cochise, "Clear" 65
1015 0 None ~~3~~4 14°C 3-W 14% 5200 ~~60~~

02-24-16 Cochise, Clear 65
1245 0 None 2 21°C 6% 5000 ~~60~~
No direct sign of impact from previous night operation.

01-24-16 Cochise, Clear 65
1600 0 None ~~2~~ ~~21~~°C ~~16~~°C 5000 ~~60~~
8 19 10

Therefore, what we actually have is a situation of

$$\frac{13.5(2) + 10.5(20.4)}{24} = 10.0 \text{ PM}$$

This is certainly interesting.
What if it were @ 5PM 2.5 for baseline
Actually, midway @ 6 is even better.

$$\frac{13.5(6) + 10.5(20.A)}{24} = 12.3$$

Which is just exactly about the limit of EPA
So you would never know anything is happening.

1 hr @ 100 = 100 additional PM2.5·hr units

Note New Unit — This is a useful unit: PM2.5·hr

10.5hrs @ 20.A = 214.2 PM2.5·hr units.

PM 2.5·hr units are what matters

Reference — EPA Exposure 12(365)24hr = 105120 PM2.5·hr units

Now assume we have
(20.4 PM)(10.5hrs)(36.5days) = 7818 PM2.5·hr units
This represents an additional exposure of 7.4% PM 2.5 increase annually.

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But in terms of more realistic numbers, the
base exposure is no more than 6 PM ~~12.5~~ 2.5
so
6(365)(24hr) = 52560 PM·hr
and 7818 PM·hr increase @ (20.4)(10.5hrs) 36.5 days is a
(7818/52560) = 15% increased load of pollution.
What we really want to do is translate into mortality.

Two scenarios: 10 87,600
~~8~~ PM Constant : ~~8~~(365)(24hr) = ~~78,840~~ PM·hr
10 $\bar{x}$ = ~~9~~ PM/24hrs
Now assume 10
23hrs@5 and 1hr@100 : (every day) 86,870
[(~~5~~)(23hrs) + 100(1)]·365 = ~~78,475~~ PM·hr
6 $\bar{x}$ = ~~9~~ 10 PM
so total exposure here is the same.

But: every day you have a $\frac{100}{10}$ = 10 times the exposure for 1 hr.

Let's translate this into mortality
This is a difference of 90 ug/m³ for 1 hr each day. (365 days)

Now, this is equivalent to 365/24 = 15.2 days per year of 90 ug/m³. This is equivalent to 30.4 days of 45 ug/m³.
This leads to a mortality increase of
$M_{10}\%$ = .007(30.4) + .48(ln 30.4) + 1.65 = 3.50%
But we have 45/10 = 4.5 therefore
(4.5)(3.5%) = 15.8% increase in mortality.

Obviously very significant.

The value, of course, is highly significant.
This would lead to

.158 (~~272~~ 2596993) = 410,325
undetected deaths per year.
This exceeds the third leading cause of death (COPD), immediately following that of heart disease and cancer.

Notice the CDC list is not complete.
Σ: 1,911,311 vs 2596993 (74% of total)

So this is a phenomenal result.

Now let's look @ our actual data:
3rd scenario therefore is:
(~~6~~ 10 PM2.5 * 24 hrs)(365) = 87,600 PM.hr

* The new unit of significance is (PM2.5 · hr)

vs

~~(13.5 hrs)(10 PM25)~~ (10.5 hrs)(20.4) PM = 214.2 PM.hr additional per day
vs
13.5 hrs @ 10 = 135 PM.hr
This is a ratio of $\frac{214.2}{135}$ = 1.59 of the original exposure.

the daily average = $\frac{(10.5)(20.4) + (13.5)(10)}{24}$ = 14.6 per day instead of 10

Assume now 10% of year = 36.5 days

The exposure rate

$M_{10}^{\%} = .007(\overset{36.5}{\cancel{30.4}}) + .48\ln(36.5) + 1.65 = 3.63^{\%}$

Estimated Mortality per $\Delta 10\,\mu g/m^3$

We have a factor of 1.59 ∼ $1.59(3.63) = 5.8\%\ (5.77)$

Mortality increase per $10^{\%}$ of year actual data.

The delta here is $5.77\% - 3.63\% = 2.14\%$

Actual increase in mortality

$.0214(2596993) = 55{,}576$ deaths.

This is very close to influenza rank.

This is relative to a baseline value of polluted air @ $10\,\mu g/m^3$.

We know from direct measurement that clean air is actually ∼ 2 PM2.5

Now let's look @ the problem in relationship to clean air

This ~~situation~~ is:

$(24\text{hrs})(2\text{PM}) = 48\ \text{PM}\cdot\text{hr}$

vs

$13.5(2) + 10.5(20.4) = 241.2$ $\qquad \frac{241.2}{48} = 5.0$

On the days that this occurs it is a

So during the time frame we'll have a fivefold increase in exposure levels.

Now if this were to happen 36.5 days per year we days have an equivalent fulltime exposure of $\frac{10.5\text{hrs}}{24\text{hrs}}(36.5) = 16.0$

Therefore our mortality ratio is

$\text{Mortality}_{10}^{\%} = .007(16.0) + 0.48\ln(16) + 1.65 = 3.1^{\%}$

but we have a ratio of $\frac{20.4}{2} = 10.2$

But something here is very wrong.
By this reasoning, you would have a

$(10.2)(3.1\%) = 31.62\%$ increase in mortality.
And maybe that is true but it is an
increase of 31.6% from a baseline of 2PM;
which is essentially nothing. So a 32% increase
over nothing is still nothing.

So the reasoning process is flawed and
does not work.

It is true that we have a fivefold exposure
risk on the days that it happens. But
Compared to what is the question?
~~Also~~ This is compared to a baseline of 2PM.
Since we know it is a 20.4 PM average increase
on those days for a 10.5 hr period
We know that $M_{10}\%$ is increased by a factor
of ~2 however it is only for the proportional
time of 10.5 hrs.
So the real question is: How many days
does it equate? Assume 10% Coverage.
So $36.5 \text{ days} \left(\frac{10.5}{24}\right) = 16$ days instead of 36.5

Now we can proceed:
reference: $\text{Mortality}_{10}\% = .007(16) + .48\ln(16) + 1.65 = 3.1\%$

1. Error on <u>Death</u> Type No! - Fix it

2. Also check $M_{10}^{\%}$ equation. Page 326

but here is our kicker solution.
We have an equivalent concentration on those days of the 20.4 ug/m3.
This leads to a Δ of $20.4 - 2 = 18.4$ ug/m3
this is therefore equivalent to
$\frac{18.4}{10} = 1.84$ ratio Average works for equally weighted data

Therefore our mortality rate increase is expected to be

$1.84(3.1)\% = \underline{\underline{5.7\%}}$ and this is calculatic.

Therefore we can now estimate the no. of deaths as
$.057(2596993) = 148,028$ deaths almost identical to COPD

Reference Scenario:
Now, we need to revisit our 1 hr 100 exposure problem
1. Every day we have 10 even $\bar{X} = 10$ per day.
within EPA standards.

2. Every day we have 6 PM 2.5 for 23 hrs 100 PM for 1 hr
$\bar{X} = \frac{6(23) + 100(1)}{24} \cong 9.9 \cong 10$ per day
w/in EPA Standards.

However.
With latter scenario we have a significant increase in short term exposure mortality that is completely transparent within the EPA Standards
Recall $Mortality_{10}^{\%} = .007(365) + .48\ln(365) + 1.65 = 7.0\%$
Now $365\left(\frac{1}{24}\right) = 15.2$ equivalent days of 90 ug/m^3 additional. This is equivalent to $\cancel{\frac{90\,ug/m^2}{15.2\,days} = \frac{20}{X}}$ X=
$\frac{90}{20}(15.2) = 68.4$ days of 20 ug/m^3
$Mortality_{10}^{\%} = .007(68.4) + .48\ln(68.4) + 1.65 = 4.16\%$ increase
but $\frac{20}{10} = 2$ Factor $2(4.16) = 8.3\%$ Increase in Mortality

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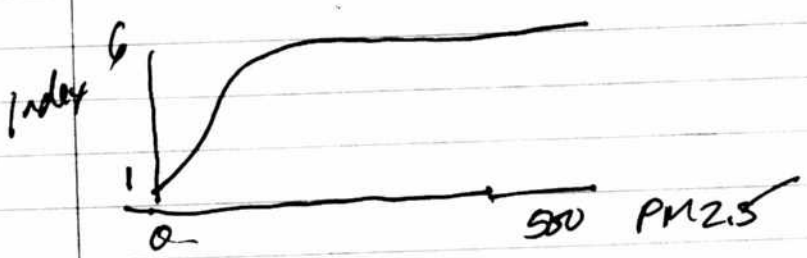
and .083(2596 993) = 215,550
additional deaths.
Which exceeds
5th & 6th leading cause of death per
year, ie, more than half the deaths
of stroke and Alzheimer's combined.

Feb 13 2016

Lets look @ an alternative index based on integration
Assume we have a logistic curve of

$$\overline{\text{Mean}}_{OM_6+EU_6+UK_6} = \frac{6.03}{1+5.65e^{-.046PM2.5}}$$



Almost all the effect is by PM2.5 = 150.
by 100 it is mostly done

$$y' = \frac{ae^{bx}}{c\cdot(d\cdot e^{bx}+f)^2}$$

that is certainly complicated enough.

			Area
>150	10		
>100	9	10	2404.8
>80-100	8	9	~~54.1~~ 110.4
>70	7	8	51.1
>60	6	7	46.9
>50	5	6	41.5
>40	4	5	35.2
>30	3	4	28.3
>20	2	3	21.6
>10	1	2	15.8
<10	0	1	11.03

a cubic fits this data quite well.

That really is a most simple scale.

#40 01/17 Document the most extreme event
01/10 #41
01/19 #42-53

VIS	Clear	Stratus, Offshore Cumulo Stratus	Sign. Aerosol / operation
	17	18	19
Visibility	60	60	30
0915			2.0
0930	2		
1000		2	
1100			8
1245			15
1415			40
1445			45
1515			52
1525			57
1630			36
1730			5
1800			2
1900			2

Feb 14, 2016

The topic of an "implicit function" and that of differentiating implicitly is an interesting topic?

How do you know if you have an implicit function or not? Lomen's paragraph on p 86 is a really interesting set of statements acknowledging uncertainty in the business.

Schaum's Calculus p 88 & p 394 has some discussion of the topic.
Notice on page 88 the use of the word "perhaps".

Schaum says an equation of the form $f(x,y) = 0$ is "said to define y "implicitly" as a function of x.
Notice the interesting language being used here,
No wonder that it was always confusing to you.
You had a right to be confused, the language is ambiguous even within the "definition"!

"Think of y as a function of x"
Differentiate both sides of the equation w.r.t. x.

p 395 "implicitly" was defined "intuitively" on p 88
Notice the continuation of ambiguous language.

The whole entire method may well be valid only over certain ranges of variables.

So no wonder this was never very certain to you.

Now that we know that the process is ambiguous, to say the least, we can proceed with Lomen on p 86.

What he is doing here is quite interesting. He is taking a function that is too difficult to solve.

Then he "assumes" that, or at least tries to assume that the function is an implicit one and then he DIFFERENTIATES IT using implicit differentiation to CREATE a differential equation that is a "transformed" version of the original equation.

Then he solves the differential equation to get the solution we need for y.

This is a fascinating discussion and approach. It means that you do not always need to investigate y(x) as your primary form

BUT THAT YOU CAN ALTERNATIVELY INVESTIGATE y'

This really is quite interesting. ! !

Developing a DQ - Fantastic!
From Data

page 332

Now, the section we really want to progress to is p145 Lomen called "Deriving Diff Eq from Data"
This is right up our alley!

Ok, we have a great example. Temperature data collected.
No regression fits well! You could use exponential ~~[illegible]~~ but we see that the is more involved, matrix set up, MCAD dependence, etc.

Knowledge of diff eqs may help us to derive an equation.
Thus is very much worth studying. Regression does not always work! Like our EPA weighting function!

method: we try to find
$\frac{\Delta T}{\Delta t} = f(t,T)$ This is the method.

We start by looking @
$\frac{\Delta T}{\Delta t} = f(t)$ and $\frac{\Delta T}{\Delta t} = f(T)$
by computing & plotting it & looking for relationships.
Spreadsheet might be easier.

You can easily move data in Casio regression module into the spreadsheet by exporting & importing CSV!

$E = \frac{\Delta T}{\Delta t}$ so look@ $E = f(A)$
$E = f(B)$

$C = \Delta t$ $A = t$

$D = \Delta T$ $B = T$

$\frac{\Delta T}{\Delta t} = f(t)$ looks exponential

$\frac{\Delta T}{\Delta t} = f(T)$ looks linear

So we do indeed see that we have something.

$\overset{x}{}$ $\overset{y}{}$

$$\frac{\Delta T}{\Delta t} = \text{[illegible]}\, T$$

So you really do not know what is x & what is y.!

or

~~$\frac{\Delta T}{\Delta t} = -8.02T$~~

We want $Y = f(x)$

$T($~~[illegible]~~$) =$

$$-8.04\left(\frac{\Delta T}{\Delta t}\right) + 34.1 = f(T)$$

$r^2 = .99$

$$\frac{dy}{dx} = f(y)$$

We can match Lower with

$X = T$

$Y = \frac{\Delta T}{\Delta x}$

so

$$\frac{\Delta T}{\Delta x} \cong -0.12T + 4.19 \quad r^2 = .99$$

Lower Law $\frac{\Delta T}{\Delta x} \cong -0.14T + 4.78$

Casio handle this fine good to learn. Now proceed.

We still have work to do.

Casio will solve this Dive w/ a single condition

You have missed some very important things here, back up.

so now we are on the right track. $\int \frac{1}{x} dx = \ln(x) + c$

we have form

$\frac{dy}{dx} = ay + b$ and thus $\frac{dy}{ay} = b\,dx$

or $\frac{1}{ay} dy = b\,dx$

The actual solution will be

$T = T_0 + (T_0 - T_a) e^{kt}$

or $\int \frac{1}{y} dx = \int b\,dx$

or $\ln y = bx$

$y = e^{bx} + c_1$

when $t = 0$, $T = 32.78$

or in this case $T = C_1 e^{bt} + C_2$

So $T = 32.78 e^{bt}$

when $T = 34.05$, $t = 20$

$34.05 = 32.78 e^{b \cdot 20}$

an $e^{b \cdot 20} = 1.0387$

This is close but I am not so sure that it is close enough

$b \cdot 20 = .0380$

$b = 1.898E-3$

So $T \tilde{=} 32.78 e^{1.898E-3 \cdot t}$

$T = C_1 + C_2 e^{-x \cdot a}$ would work fine.

Your regression does not work ~~for~~ because of extra constants

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One of the things that you are learning here is that you can seek a differential relationship if common regressions do not work.
But you know that you can also seek exponential harmonics.

We agree that we have

$$\frac{\Delta T}{\Delta t} = aT + b$$

One of the apparent conditions is that $a < 0$.

Next the equilibrium solution become important. Notice that this is an autonomous form, so we set

$$aT + b = 0 \quad \Rightarrow aT = -b \text{ or } T = \frac{-b}{a}$$

~~a b=~~. I think we should understand equilibrium solutions better. Can we plot a phase line? What does it mean here?
How does anyone know to manipulate this equation further?

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The simplest of developed differential equation is bringing up all kinds of interesting situations.

We all agree that there is a relationship of
$\frac{\Delta T}{\Delta t} = aT + b$ my coefficients by regression are
$a = -0.126$ $a = -0.14$
$b = 4.19$ $b = 4.78$

His coefficients are
Why the difference? He used Central differences, I used the simpler forward difference.
Let's go ahead w/ ours for now.

Every initial Condition creates its own solution.
We have a fair amount of error in our solution.
Let's try to work on this.

OK, we redid the regression with central difference.
We do get
$y = -0.14X + 4.76$ $r^2 = .994$
$X =$ List 5 = Temp
$Y =$ List 4 = $\Delta T / \Delta t$
and I do have the regression curve plotted OK.

So $\frac{\Delta T}{\Delta t} = -.014T + 4.76$ or $\frac{dT}{dt} \overset{\sim}{=} -.014T + 4.76$

This does indeed give a much better solution numerically w/ less error.
Let's plot 3 different initial Conditions.

Interestingly but IC @ $x=20$ gives a false solution? Why?
IC's @ $x=0$ and $x=10$ are fine but not $x=20$ or 18
So for some reason we can not go backwards w/ the solution.

We do have a good [illegible] numerical solution now. It does have error but it is quite manageable and within measurement errors.

Now, what do we do with it is the question?

1. We can accept the numerical solution, take values from it, and attempt to construct a regression from it.
   But a standard regression won't work well
   In which case we could have constructed a regression to begin w/ w/ the raw data.

2. The value of the differential ~~sets~~ examination is that we have discovered a linear relationship between $\frac{\Delta T}{\Delta t}$ and T. This is invaluable and is the main value here. If it is linear then you should be able to come up w/ a closed solution. So this could be worth the investigation in itself.

3. Indeed you do realize how valuable your exponential harmonic series is now. You should be able to model most any data that is out there. This is huge.

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Now that we know our verification, that we have less error, and that central difference formula really does appear to be superior, and that a linear relationship does exist, let's look @ how we go about the closed solution. He played a trick which helps to gain even further insight but let's take our solution as it is.

$$\frac{dT}{dt} \overset{?}{=} -.014T + 4.76$$

this is separable and we should be able to solve it.

$$\frac{dT}{-.014T+4.76} = dt$$

$$\int \left(\frac{1}{-.014T+4.76}\right) dT = \int dt$$

So $+4.76$ This is your error!

$$\frac{1}{-.014}\ln(-.014T) + C_1 = t$$

$$\ln(-.014T) = -.014t - C_1$$

$$-.014T = e^{-.014t - C_1}$$

$$-.014T = C_1 e^{-.014t}$$

$$T = C_1 e^{-.014t}$$

$$\int \frac{1}{u}\,du = \ln u + C$$

$$u = -.014T + 4.76$$

$$du = -.014\,dT$$

or

$$\frac{1}{-.014}\int \frac{1}{-.014T+4.76}(-.014)\,dT$$

$$= \frac{1}{-.014}\ln(-.014T) + C_1$$

$$\boxed{\text{So } \frac{1}{-.014}\ln|-.014T+b| + C_1 = t}$$

$$\int \frac{1}{ax+b}\,dx \; ? \quad = \frac{1}{a}\ln|ax+b| + C$$

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We were on the right track.

$$\frac{1}{-.014}\ln|-.014T+4.76|+C_1=t$$

$$\ln|-.014T+4.76| = -.014t - C_1$$

$$|-.014T+4.76| = e^{(-.014t-C_1)}$$

$$-.014T+4.76 = C_1e^{-.014t}$$

$$-.014T = C_1e^{-.014t} - 4.76$$

$T = C_1e^{-.014t}+340$ Not looking good.

When $t=0$, $T=32.78$

$T = C_1+340$

$32.78 = C_1+340$ $C_1 = -307.22$

$T=-307.22e^{-.014t}+340$ This is not working. Why?

The actual answer is

$T = 34.14 - e^{.308-.135t}$

We are on the right track. Let's work this out.

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We apparently shouldnt be looking @ the equilibrium points.

$$\frac{dT}{dt} \cong -.014T + 4.76$$

$$-.014T + 4.76 = 0$$

$$T = \frac{-4.76}{-.014} = 340?$$

Visibiliti
40/60 ratio
Decrease

All visibility will be scaled by ~~40/60~~
Logistic regression

~~01~~ 02-25-16 City of Rocks State Park, NM, Clear
2215 0 None ~~8~~6 14°C ~~0-NA~~ 2-SE 10% ~5000'? 65

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~~01-25-16~~ 01-26-16 City of Rocks, NM, Clear
1100 0 None 10 19°C 0-NA 10% ~5000'? 65

Feb /

Note: w/ reference value available @
City of Rock State Park all visibility
readings will be decreased by a ratio of
40/60. A consistent pattern of increased
concentrations to south over
lower regions and population
center of Phoenix & Tucson

~~01-25-16~~ 01-26-16 City of Rocks State Park. Modest Haze to N. Clear Significant Haze to S
1400 0 None 8 22°C 1-SE 5% 5200' 65
Cablabrated Visibility by 40/60 ratio

Feb /

01-26-16 City of Rocks, Clear
2215 0 None 8 15°C 0-NA 13% 5200' 65

01-27-16 City of Rocks, ~~Pa~~ Mostly Sunny
Increasing Haze & Cirro Stratus Banks
1530 0 Light 25 27°C 4-SW 3% 5200 55
Light Aerosol Trails Active

Feb /

~~01~~-27-16 City of Rocks, NM Partial Diffuse Cirrostratus
Coverage to E, Clear but dimished night star visibility.
1915 0 None 9 18°C 2-SW 5% 5200 55

01-28-16 City of Rocks, Clear
1000 0 None 10 20°C 2-SW 5% 5200 55

PM2.5 #9

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Feb

01-28-16 City of Rocks, Clear
1745 0 None 10 21°C 3-SW 4% 5200' 55

Diffuse Cirro Stratus
01-29-16 City of Rocks, Mostly Sunny, Active Operation to S.
0815 0 Moderate 6 13°C 2-NE 20% 5200' 55 to N
Traffic is heaviest to South. E-W alignment 35 to S
Substantial ~~Considerable~~ aerosol banks to S. & E. Border Area looks as largest

01-29-16 Silver City NM, Mostly Sunny, Overhead Haze
1130 2 None 32 25°C 3-NW 3% 6000' 50

Feb

01-29-16 City of Rocks, Partly Sunny, Diffuse
Cirro Stratus, Cirro Cumulus & Amorphous
1515 0 None 20 24°C 7-NW 4% 5200 40-E-S 50-N-W
Impact of Aerosol operation clearly evident, diminished visibility, amorphous haze & cloud cover

~@ Approx 2130 the Orange lights ~~see~~ observed again
~ ~~N45E~~ N65E ~100 mi ± 20 miles
~2° above horizon. Best location estimate: White Sands Space Port

Feb

Haze to ground level
03-01-16 City of Rocks, Mostly Sunny, Diffuse
Cirrus ~~Haze~~ Stratus Haze across majority of sky.
0800 0 None 8 13°C 1-NE 25% 5200' 40
Impact of Aerosol operation remains evident.

March 2016

03-01-16 City of Rocks, same as previous
0930 0 None 12 20°C 1-NE 20% 5200 40

03-01-16 Same
1345 0 None 32 28°C 5-SE 3%

~~0302-06~~ 03-02-06 Same, SE
1515 0 None 37 30°C 6-~~NW~~ 3% 5200 40

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~~01-25-16~~ City of Rocks State Park, Clear
~~2215 0 None~~

03-03-16 City of Rocks, Partly Sunny,
Diffuse Cirro Stratus, Extensive Haze all Quadrants, Active Aerosol Operation
0800 0 Moderate [illegible]9 15° 1-SE 18% 5200 ~~40~~ 35

03-03-16 City of Rocks ~~Mostly~~ Partly Sunny, Same as above
1115 0 Moderate 20 25° 2-SE 5% 5200 ~~40~~ 35

03-03-16 City of Rocks Extensive Haze, Cirro Stratus
all quadrants, Mostly Cloudy
1400 0 None 150 32°C 4-SE 3% 5200 ~~40~~ 35

Mostly Diffuse a 90%
03-03-16 City of Rocks Cldy, Cirro Stratus ~~90~~% Coverage
1545 0 None 25 28°C 2-SW 3% 5200 45

03-04-16 City of Rocks. Major Aerosol Op in Progress.
Full Coverage ~~Extensive~~ Cirro Stratus Blanket & Haze in all Quadrants
0800 0 Heavy 10 15°C 1-NE 14% 5200 ~~35~~ 30

03-04-16 City of Rocks, Partly Sunny, Extensive Haze
& Cirro Stratus all quadrants
0915 0 Moderate 20 23°C 2-SE 3% 5200 30
Active Aerosol Operation now primarily to S.

03-04-16 ~~1300~~ City of Rocks, ~~Par~~ Same as above
1300 0 Light 35 28°C 0-NA 3% 5200 30

03-04-16 City of Rocks, Partly Sunny, Extensive
Cirro Stratus & Haze bank to S. towards border region
1530 0 Light 40 30°C 3-NW 3% 5200 30
Clearing overhead & to N.

PM2.5 #9
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Diffuse

03-05-16 City of Rocks. Partly Sunny. Extensive Cirro Stratus, Cirro Cumulus & Haze in all quadrants. Aerosol Op remains in progress. Op appears to be in advance of approaching moisture / potential Storm front.
0930 0 Moderate 8 21°C 4-SE 4% 5200 25

03-05-16 City of Rocks, Same as above
1345 0 None 45 30°C 5-SW 3% 5200 25