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A Release of Internal Original Research Documents

Authored
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Chemistry Vol XVI

MICRO - PERFORATED SHEETS

120
SHEETS
FEUILLES

3 SUBJECT COLLEGE RULED
NOTEBOOK
CAHIER DE NOTES
À 3 SUJETS LIGNES MOYENNES

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Chemistry - Lab Notes
Aug 2016
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Aug 18 2016 Priest Lake, Idaho

On the lake for the next two weeks. Many projects as usual. Lets start w/ the vapor pressure regression model.
We have a model for molecular wt:

$$MW^* \cong \ln(tr) + \frac{6.265}{.069}E\text{-}3T + 1.506$$

or

$$tr^* \cong e^{(.069MW^* - 6.265E\text{-}3T - 1.506)}$$

T in °C
MW in gms/mole
tr in minutes

Hayes Sep D Column.

$n \cong 35$
$\sigma_s^2 = 0.29$

The good news is that this is also a self improving model.

The model is used to predict the next outliers and unknowns.

Once confirmed, the additional species are added to and improve the model further.

$$\ln(tr) \cong C_1 \cdot T + C_2 \cdot MW + C_0$$

or

$$tr_{MW} \cong e^{(C_1 T + C_2 \cdot MW + C_0)} \text{ or } tr = e_{MW}^{(C_1 \cdot T + C_2 VP + C_0)}$$

Before creating a vapor pressure model, we should continue to improve the molecular weight model.

New species:

Species	T	MW	Coeff	tr	ln(tr)
Propane	80°	44.1	1	4.12	
Propene	80°	42.1	1	5.12	
Butane	80°	58.12	1	9.57	
Propane	150°	44.1	1	1.24	
Propene	150°	42.1	1	1.36	
Ethane	150°	30.07	1	0.70	

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Lets make some predictions for 220°C

$tr^* = e^{(.069MW^* - 6.265E{-3}T - 1.506)}$

let $T = 220°C$

Propane 44.10 $tr^* = 1.17$ meas 1.24

Propene 42.08 $tr^* = 1.02$ meas 1.36

The double bond Contra indicates.
No solution for this yet.

Revise the model to eliminate data points
23 & 24.

$$MW^* = \frac{\ln(tr) - C_1T - C_0}{C_2}$$

Revised Model w/ 23 & 24 removed:

$C_1 = -6.201E{-3}$
$C_2 = .071$
$C_3 = -1.584$

$\sigma_s^2 = 0.29$

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Therefore the adjusted Molecular Wgt Model is now:

$$MW^* = \ln(t_r) + \frac{6.201E-3}{.011}T + 1.584$$

or

$$t_r^* \approx e^{(.011\,MW^* - 6.201E-3T - 1.584)}$$

and $\sigma_s^2 = 0.29$

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Vapor Pressure Data

Species		T	VP p 6-66 CRC	Coeff	t_r	$\ln(t_r)$
Propane	1	80°C	-42.3		4.25	1.45 ✓
	2	80°C	-42.3		3.79	1.33 ✓
	3	80°C	-42.3		3.56	1.27 ✓
	4	80°C	-42.3		4.1	1.41 ✓
	5	150°C	-42.3		1.1	.095 ✓
	6	220°C	-42.3		1.04	.039 ✓
	7	150°	-42.3		1.19	.171 ✓
Butane	8	80	-.8		11.5	2.44 ✓
	9	80	-.8		10	2.30 ✓
NO		~~150~~			? ~~2.343~~	—
	10	220	-.8		2.19	.782 ✓
	11	150	-.8		4.42	1.485 ✓
	12	80	-.8		9.4	2.24 ✓
Propene	13	150°	-47.9		1.78	.578 ✓
	14	150	-47.9		2.34	.851 ✓
Ethane	15	150°	-88.8		0.70	-.357 ✓
	16	80	-88.8		1.36	.307 ✓
	17	220°	-88.8		0.48	-.728 ✓
CO_2	18	220°C	-78.6		0.84	-.174
	19	80°	-78.6		1.73	.548
CO	20	220°	-191.7		4.27	1.452

Found major omission in entry of data
for the VP model. Now corrected.

We apparently want VP @ 0°C @ 100 KPA
This is on p 6-66 of CRC Handbook.
Dipole moments (Polarity) in M/D might be next
~~This is~~ on p 9-44 CRC Handbook.

Corrected Coefficients

For n = 20 model results are

-7.77E-3 $C_1 =$ ~~-9.58E-3~~
+ 4.682E-3 $C_2 =$ ~~2.842E-3~~
+ 2.168 $C_3 =$ ~~2.139~~ and $\sigma_s^2 =$ ~~0.521~~ .497

This means that we now have 2 different methods of predicting the tr, MW or vapor pressure.
Our model here is

$$VP^* \approx \frac{\ln(tr) + \overset{7.77E-3T - 2.168}{\cancel{9.58E-3T - 2.139}}}{\cancel{2.842E-3}\ 4.682E-3}$$

Major

or

$$tr \approx e^{\overset{(4.682E-3 \cdot VP - 7.77E-3 \cdot T + 2.168}{(\cancel{2.842E-3} \cdot VP - \cancel{9.58E-3T} + \cancel{2.139})}}$$

And we can weight our final solution by the variance

$$9 \quad tr_{combined} = \frac{\frac{1}{\sigma^2_{MW}} \cdot \hat{tr}_{MW} + \frac{1}{\sigma^2_{VP}} \cdot \hat{tr}_{VP}}{1/\sigma^2_{MW} + 1/\sigma^2_{VP}}$$

$$\ln(tr) = 2.842E-3VP / 9.58E-3T - 2.139$$

$$tr = e^{(2.842E-3 \cdot VP - 9.58E-3T - 2.139)}$$

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Vapor Pressure Data (cont)

Lets put this into practice between

Propane w/ CEC Hair 80°C
Propene
& Butane, & CO_2

				$1/\sigma^2$ 3.45	2.01		
				(0.29)	(0.497)		Actual
X_{wgt}		MW	VP	tr_{MW}	tr_{VP}	X	
3.20	Propane	44.10	-42.3	2.82	3.85	~~3.06~~	4.12
2.93	Propene	42.08	-47.9	2.45	3.75	~~2.80~~	5.12
6.40	Butane	58.12	-.8	1.41	4.68	~~6.17~~	9.57
2.96	CO_2	44.01	-78.6	2.80	3.25	~~2.93~~	1.61
1.35	CO	28.01	-191.7	1.02	1.91		

$$tr^*_{MW} = e^{(.069\,MW^* - 6.265E-3T - 1.506)}$$

$$tr^*_{VP} = e^{\overset{4.682E-3VP - 7.77E-3T + 2.168)}{\cancel{(2.812E-3\,VP - 9.58E-3T + 2.139)}}}$$

Predict @ 80°C

Something still seems wrong w/ this.
VP model does not look good @ all.

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Something is wrong w/ the VP model.

We have a major flaw in the model.
The higher the vapor pressure, the more slowly it elutes. The lower the pressure, the more quickly it elutes.

Which is correct, but obviously polar molecules are behaving entirely differently.

Also alkenes are behaving entirely different from alkanes.

These differences are causing a lot of problems in the model.

Double & triple bonds are increasing the time, not decreasing it.
eg alkenes, alkynes.

Is our term the Vapor Pressure by the Polarity?

Species	VP	Polarity ~~Molarity~~	VP · Polarity ~~Molarity~~	
Propane	-42.3	.084	-3.55	4
Propene	-47.9	~~3.17~~ NO!	-151.84	1
Butane	-.8	.132	-.196	5
CO_2	-~~78~~ 78.6	0	0	6
CO	-191.7	.11	-21.09	2
Butene	-21.09	.503	-10.6	3

Ok, our model has a problem.

It seems to me our model should be of the form

$$\ln(tr) = C_1 \cdot MW + C_2 \cdot VP + C_3 \cdot DP + C_4 T + C_5$$

However prediction capability has to be equal to

~~$\ln(tr) = C_1 \cdot \text{Single Variable} + C_2$~~

$$\ln(tr) = C_1 \cdot T + C_2 \cdot \text{Single Variable} + C_3$$

Your theory is that the ~~sum~~ average of individual regression should get you closer to the truth, especially when weighted by the variance.

But VP seems to introduce some real problem.

1. Molecular Weight
2. Vapor Pressure
3. Polarity (no of bonds).

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I think that the first stage is to determine if the model has any theoretical validity.

We can do this by comparing GC data w/ actual physical known values.

			C_1	C_2	C_3	C_4	C_5		
BP		Species	MW	VP	DP	T	1	tr	ln(tr)
-44	1	Propane	44.10	-42.3	.084	80	1	3.41	1.24
-1	2	Butane	58.12	-.8	.132	80	1	9.30	2.23
-1	3	Butane	58.12	-.8	.132	80	1	9.64	2.26
-44	4	Propane	44.10	-42.3	.084	80	1	3.56	1.27
-88	5	CO_2	44.01	-78.6	0	80	1	1.62	0.48
-88	6	CO_2	44.01	-78.6	0	60	1	2.60	0.96
-88	7	CO_2	44.01	-78.6	0	100	1	1.19	0.17
-88	8	CO_2	44.01	-78.6	0	120	1	0.94	-.06
	9	H_2	2	-252.8	0	40		0.28	-1.27
[illegible]	10	O_2	32	-183.1	0	40		0.39	-0.94
	11	N_2	28	-195.9	0	40		0.39	-0.94
	12	O_2	32	-183.1	0	120		0.36	-1.02
	13	N_2	28	-195.9	0	120		0.36	-1.02
-88	14	CO_2	44.01	-78.6	0	40		3.93	1.37
-88	15	CO_2	44.01	-78.6	0	60		2.57	0.94
-44	16	Propane	44.10	-42.3	.084	80		4.25	1.45
-44	17	Propane	44.10	-42.3	.084	80		3.79	1.33
-1	18	Butane	58.12	-.8	.132	80		9.40	2.24
	19	Ethane	30.07	-88.0	0	80		1.33	0.28
	20	CO	28.01	-191.7	.11	80		4.27	1.45
-44	21	Propane	44.10	-42.3	.084	80		4.0	1.39
-1	22	Butane	58.1	-.8	.132	80		10	2.30
	23	Butene	56.1	117.2 -6.6	.503	80		13.03	2.57

check MW reversed

		a	b	c	d	e			
BP		Species	MW	VP	DP	T	1	tr	ln(tr)
	24	Propene ✗	✓ 42.08 44.10	47.9 -42.3 ✓	.366 ✗	150 ✓		1.78	0.58 ✓
-44	25	Propane ✓	44.10	OK -42.3 ✓	.084 ✓	150 ✓		1.88	0.63 ✓
	26	Ethane	✓ 30.07	-88.8 ✓	0 ✓	220 ✓		0.48	-.73 ✓
-88	27	CO_2	✓ 44.01	-78.6 ✓	0 ✓	220 ✓		0.84	-.17 ✓
-44	28	Propane	✓ 44.10	OK -42.3 ✓	.084 ✓	220 ✓		1.04	+.04 ✓
	29	Propene	✓ 42.08	-47.9 ✓	.366 ✓	220 ✓		1.37	.31 ✓
-1	30	Butane	✓ 58.12	-.8 ✓	.132 ✓	220 ✓		2.19	0.78 ✓
	31	Butene	✓ 56.1	-6.6 / 17.2	.503	220 ✓		2.79	1.03
	32	Propene	✓ 42.08	-47.9 ✓	.366	80		5.12	1.63
	33	Ethane	✓ 30.07	-88.8 ✓	0	80		1.36	.31
-88	34	CO_2	✓ 44.01	-78.6 ✓	0	80		1.61	.48
-44	35	Propane	✓ 44.10	-42.3 ✓	.084	80		4.12	1.42
-1	36	Butane	✓ 58.12	-.8	.132	80		9.57	2.26

You had an error of the error determination:

$\sigma_s^2 = 0.225$ (Very good!)

~~$\sigma_s^2 = .354$~~ $n = 36$ ~~($\sigma_s^2 = 0.58$)~~

The model is:

$$\ln(t_r) = .04\,MW + 5.583E{-3}\,VP + 1.06\,DP - 8.677E{-3}\,T + 0.242$$

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I now have the means to create separate models for MW, VP, & DP

Let's start w/ the MW model.

We can simply remove columns from the regression matrix. [B]

$[MW \quad VP \quad DP \quad T \quad 1] \quad [e]$

MW: $\ln(t_r) = .076MW - 7.052E\text{-}3T - 1.743$

$\sigma_s^2 = 0.48 \qquad 1/\sigma^2 = 2.08 \qquad \sigma = .69$

$t^*_{r_{MW}} = e^{(.076MW - 7.052E\text{-}3T - 1.743)}$

Best regression

VP: $\ln(t_r) = .012VP - 8.931E\text{-}3T + 2.488.$

$\sigma^2 = 0.365 \qquad 1/\sigma^2 = 2.74 \qquad \sigma = .60$

$t_{r_{VP}} = e^{(.012VP - 8.931E\text{-}3T + 2.488)}$

DP: $\ln(t_r) = 4.414DP - 7.545E\text{-}3T + 1.102$

$\sigma^2 = 1.004 \qquad 1/\sigma^2 = 1.00 \qquad \sigma = 1.00$

$t_{r_{DP}} = e^{(4.414DP - 7.545E\text{-}3T + 1.102)}$

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In Casio Spreadsheet, the weighted mean is:

$$N = \frac{\overset{L}{\cancel{K}}2 * \overset{F}{\cancel{E}}2 + \overset{M}{\cancel{L}}2 * \overset{G}{\cancel{F}}2 + \overset{N}{\cancel{M}}2 * \overset{H}{\cancel{G}}2}{\underset{L}{\cancel{K}}2 + \underset{M}{\cancel{L}}2 + \underset{N}{\cancel{M}}2}$$

We have simulated a Complete mystery substance @ 80°C

$t_r \cong 3.0$ min

Therefore
$MW^* \cong 45$
Vapor Pressure $\cong -55$
Polarity $\cong 0.13$ $t_r \cong 3.02$

Propane or CO_2 appear to be Candidates.

Propane $(45-44.1)^2+(55-42.3)^2+(.13-.094)^2 = 162.10$

CO_2 $(45-44.01)^2+(55-78.6)^2+(.13-0)^2 = 558.0$

Therefore the most likely material is propane.

Lets pick another.
Assume tr = 5.3min. T° = 120°C

Our mystery material has a
MW ≅ 56
Vapor Pressure ≅ +20
Polarity ≅ + 0.33

Our closest candidate appears to be butane.
MW = 58
VP = -.8
Polarity = 0.13

This actually looks pretty smart.

We can start looking @ unknowns for real.

Not only that, the model is self improving.

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Lets work w/ Hair @ 150°C

We have a $t_r = 1.24$ + $t_r = 1.36$ @ 150°C

$t_r = 1.24$:
Estimated MW = 40 VP = -80 Polarity = .05

$t_r = 1.36$
Estimate MW = 41 VP = -70 Polarity = .08

Candidates:	CO_2	44	-79	0
	Propane	44	-42	.08
	Propene	42	-40	.37

CO_2 + Propane are the most likely candidates
Probability Distribution can be used to weight the deviations

One molecule should be slightly more polar than the other. Therefore 1st peak are more likely CO_2 & 2nd peak be more likely propane.

Now ~~as~~ we go to 80°C. Two very definite peaks

	$t_r = 4.12$	$t_r = 5.12$
MW*	49	52
VP	-30	-12
Polarity	0.21	0.26
~~Still Vote~~	~~CO_2~~	~~Propane~~
Could be	Propane	Propene.

80° Column run is much more accurate
than a 150 run.
So it should be weighted accordingly also

Look @ the CO_2 peak
t_r = 1.61   T = 80°C

		Actual
MW*	≅ 37	44
VP*	≅ -110	-78
Polarity	= 0	0

This tells you the peak @ 1.61 is CO_2
The peak @ 4.12 is propane
peak @ 5.12 is propene

	CO_2		Propane
	MW	VP	DP
Measured			
Actual			

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		Actual MW	80° Calc ~~Atms~~	Actual VP	800 Calc ~~Atms~~	Actual DP	80° Calc ~~Atms~~
actual	CO_2	+44 49	37	-78 1024	-110	0 0	0
	Propane	+44 25	49	-42 144	-30	+.08 .0169	0.21
	Propane	+42 100	52	-48 1296	-12	+.37 .0121	0.26

Δ

There is some normalization required here along w/ the probability distribution, to compare.

So what you will do is take one Category @ a time. Eg MW. Use lowest temperature possible for peak @ tr=1.61 80°C

We estimate MW = 37
Now, who are the candidates

			Δ
2	CO_2	44	7
2	Propane	44	7
1	Propane	42	5

We all will have 3 deviations.
Assume max deviation represents 80° of value.

Then you need your math model.
but you can use Sigma
~~σ = 1.155~~ $\overline{\Delta}$ of $\overline{X}$ diff = 6.33

$\overline{X}$ = 43.33

Now we estimate VP
We Calculate -110

			Δ
1	CO_2	-78	~~40~~32
3	Propane	-42	68
2	Propene	-48	62

Now estimate DP
We Calculate Ø.

①	CO_2	0
②	Propane	.08
③	Propene	.37

So Σ CO_2 = 2 + 1 + 1 = 4
Σ Propane = 2 + 3 + 2 = 7
Σ Propene = 1 + 2 + 3 = 6

Therefore CO_2 wins. The lowest no. wins.

We therefore tentatively identify Peak @ 1.61 @ 80° C for human hair as CO_2

Based solely on my model vs actual properties of all candidates.

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you step through each peak in this fashion.
Eg peak @ 4.12 @ 80°C
We estimate

		Propane Δ	Propene Δ
MW^*	= 49	5 ①	7 ②
VP	-30	12 ①	~~12~~ 18 ②
polarity	= 0.21	.13 ①	.14 ②

Choices are Propane or Propene

Σ Propane = 1 + 1 + 1 = 3 Winner
Σ Propene = 2 + 2 + 2 = 6

So now we have peaks @ 1.61 & 4.12
tentatively identified @ CO_2 Propane

Now to tr = 9.57 min
MW^* = 60
VP ≅ +40
polarity = 0.40

only candidates are Butane & Butene

	Butane Δ	Butene Δ
MW	2 ①	4 ②
VP	39 ①	77 ②
Polarity	.27 ②	.10 ①
	Σ = 4	Σ = 5

Winner is Butane

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We can also look @ ethane.

Notice we are taking a complete unknown and pegging it

Let's work on the ethane & CO_2 peaks 80°C

Ethane prospect: tr = 1.36
CO_2 prospect tr. 1.61

Concentration is a joke here

for 1.36
Estimated Properties
MW = 34
VP = -122
DP -.04

for 1.61
MW 37
VP -110
DP 0

1,36 Compared to CO_2 & Ethane

Concentration speaks highly of CO_2 here

CO_2 Actual			Ethane Actual	
MW	44	②	30	①
VP	-79	②	-89	①
DP	0	⓪	0	⓪

$\Sigma = 4$

$\Sigma = 2$

Ethane Wins

Good
1.36 is Ethane

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tr = 1.61 Compared to CO_2 & Ethane

	CO_2		Ethane	
MW	7	0	7	0
VP	31	2	21	1
DP	0	0	0	0

Ethane wins again but only by one point. Concentration of [illegible] says it is CO_2.

Now we transition to 150°C hair plot.

tr = 1.84	Butane iSi	Propene
MW ≈ 45	58	42
VP ≈ -45	-.8	-48
DP ≈ +.15	.132	0.37

Candidates Propane, but you have already identified Propane. This strongly suggests propene.

150°C is not working well.
In this Case Butane is not @ all winning when it should. This shows the [illegible] of using 150°C when you have the option of 90°C. The lower the temperature the better.

This is somewhat pullometric chart 150°C to points to propane or propene when it should be butane.

Aug 19 2016   Priest Lake

We are making good progress in developing predictive capability with GC. It is working with sufficient reliability to be of value. The CASIO handles it well.

The one quirk so far is that data for a 150° Chart, presumed to be butane, did not match butane well at all, but did match propane or propene very well. But, this is very confusing.

Let's review the data for butane @ 150°C

Another advantage is that the model is self improving.

The peculiar item is that the model also predicted propane and propene very well also. This does not exactly make sense.

Well, guess what? You have no data in the system for butane @ 150°C. This is contributing to the problem.

This is a great example of the value of a self improving model.

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x

Save For Data Addition

Data addition Aug 19 2016

		Species	MW	VP	DP	T	1	tr	ln(tr)
-1	37	Butane	58.12	-.8	.132	150	1	1.9	0.64
	38	Butene	56.1	-6.6/17.2	.503	150	1	2.65	0.97

Predicted MW 48 vs formerly 45

VP -41 -45

DP = 0.15 .15

Candidates are -

so molecular wt is a little higher

vapor pressure is a little lower

DP is the same.

Actual Data

MW Butane

VP

DP

	Butane	Δ		Propene	Δ	
MW	58	10	②	42	6	①
VP	-.8	40	②	-48	7	①
DB	.132	.02	①	0.37	.22	②
		Σ =	⑤		Σ =	④

Propene still does win but it is a little better and it does not win by a whole lot.

Interesting that the dipole moment is the only winner.

Adjusted Model Results w/ Butene @ 150°C added

$n = 37$: $\sigma^2 = 0.234$

$C_1 = .035$
$C_2 = 5.99E-3$
$C_3 = 1.082$
$C_4 = -8.95E-3$
$C_5 = 0.466$

Now for individual regressions

MW:

$$tr^*_{MW} = e^{(.073 MW - 7.303E-3 T - 1.625)}$$

$$\sigma_S^2 = 0.334$$

VP:

$$tr^*_{MW} = e^{(.012 VP - 9.075E-3 T + 2.482)}$$

$$\sigma_{VP}^2 = 0.271$$

DP:

$$tr^*_{DP} = e^{(4.414 DP - 7.524E-3 T + 1.102)}$$

$$\sigma_{DP}^2 = 0.713$$

Now back to butane prediction @ 150°C we do get the same results. The results are close (ERank = 4 vs 5) but propane is still the winner.

I suspect the answer to this dilemma is over representation in the 80 degree range & under representation in the 150 degree range. Only time and additional data will improve ~~this~~ situation.

80° data : 18 data points
150° data : 3 data points.
that pretty much explains it.

Ok, lets move on. Next peak on list @ 150°C.

t_r = 2.42
Prediction
MW = 50
VP = -19
DP = .21

Recall that MW was too low for butane. Err on the high side.

Candidate
Butene
MW = 56.1
VP = ~~[illegible]~~ 117.2
DP = .503

Nothing else can fit so butene should be added as a data point for 150°C. Self improvement.

Everything is acceptable here except for Vapor pressure is way off.

We now add butene as an additional data point @ 150°C and recreate the model.

Adjusted Model $n = 38$ $\sigma_S^2 = .265$

C_1 0.043
C_2 4.501E-3
C_3 .731
C_4 -8.763E-3
C_5 .034

$\sigma_{MW}^2 = .328$ MW: $t^*_{MW} = e^{(.073MW - 7.402E-3T - 1.588)}$

$\sigma_S^2 = .319$ VP: $t^*_{VP} = e^{(.011VP - 9.101E-3T + 2.381)}$

$\sigma_S^2 = .726$ DP: $t^*_{DP} = e^{(3.851DP - 7.438E-3T + 1.125}$

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Now lets go back to Butane & Butene and see how they were affected.

Butane : tr = 1.9

		vs Actual
Now Butane becomes	MW = 46	58
	VP = -35	-.8
	DP = +0.17	.132

		vs Actual
Butene ~~Benzene~~ becomes (tr = 2.65)		
	MW = 50	56
	VP = -5	117.2
	DP = +.25	.50

Candidates are propane, butane, & butene.
Butene is closest for DP

		MW	Δ		VP	Δ		DP	Δ	Σ Ranks
Propane	①	44	(6)	②	-42	(8)	②	.08	(.17)	= 1 + 2 + 2 = 5
Butane	②	58	(8)	①	-.8	(5)	①	.13	(.12)	= 2 + 1 + 1 = ④
Butene	①	56	(6)	③	~~117~~ No! -6.4	(112)	③	.50	(.25)	= 1 + 3 + 3 = 7

Butane is the winner, but the actual answer is butene. So it is getting better but it is still falling short. We continue to need more representation of data @ 150°C but you are in the neighborhood.

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Let's go to the next peak, which surely is predictive.

t_r = 3.50

MW=55

VP = +25

DP=.33

We see that MW is pushing into new territory, so we anticipate <u>something</u> new, like pentane! Butene has an anomalous high VP, somewhat out of character. Besides butene this is the first positive vapor pressure. Also the polarity is getting higher. Let's look @ pentane

	MW	VP	DP
C_5H_{12} Pentane	72	35.7	.13
C_5H_{10} Pentene	70	29.6	0.5

VP is p 6-66
DP is p 9-44

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*

Propene VP is -47.9!!!!
Not -42.3 This should be fixed.

Butene is -6.6, not 117.2!
Fix it!!

Fix This!!!

Butane VP is -.8 Ok This was a big deal.

It is why we had a problem

I think we add new data

		Species	MW	VP	DP	T	/	tr	ln(tr)
	39	Pentane	72	35.7	.13	150	/	3.58	1.28
	40	Pentene	70	29.6	.5	150	/	4.66	1.54
add	41	Pentane	72	35.7	.13	220	1	3.4	1.22
		Hypothetical:							
C_6H_{14}	42	Hexane	86	68	0,00	220	1	7.5min	2.01

Choose tr as 0.5(9.73+4.66) = 7.20 w/model projected to 7.5 min.

Model No 5

Use This for now

The adjusted model (n= 40) is now

C_1	2.705E-3
C_2	.012
C_3	1.247
C_4	-9.57E-3
C_5	2.328

$\sigma_s^2 = .205$

This now represents an improvement w/ the error removed.

MW:

$$tr^*_{MW} = e^{(.064\,MW - 7.513E{-}3T - 1.258)}$$

$$\sigma^2_{MW} = 0.355$$

VP:

$$tr^*_{VP} = e^{(.014\,VP - 8.863E{-}3T + 2.64)}$$

$$\sigma^2_{VP} = 0.234$$

DP:

$$tr^*_{DP} = e^{(3.671\,DP - 7.136E{-}3\,T + 1.123)}$$

$$\sigma^2_{DP} = .707$$

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OK, we now have a new model that fixes an important VP error and adds C_5 date.

Lets go back to butane & butene

Butane : tr = 1.9

	Predicted		vs	Actual
	MW	47		58
Fair	VP	-47		-.8
	DP	.16		.13

	Butene : tr = 2.65		vs	Actual
	MW	53		56
very good!	VP	-25		-6.6
	DP	.26		.50

	Now Pentane tr = 3.56		vs	Actual
	MW =	57		72
still low.	VP =	-4		35.7
This is much closer to Butene	DP =	.33		.13

	Now Pentene tr = 4.66		vs	actual
	MW =	61		70
Very good.	VP =	+16		29.6
	DP =	+.41		+.5

OK, the model is now behaving quite decently up through pentene. Some weakness on butane & pentane.

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Now, for kicks, let us predict the last peak on Hair 220°C.

t_r = 328	Δ	Pentane		Δ	Pentene	
MW = 64	8	72	②	6	70	①
VP = +35	1	36	①	5	30	②
OP = +.44	.31	.13	②	.06	.5	①
		Σ Rank	$\boxed{5}$			$\boxed{4}$

Best estimate is Pentene
Which matches expectation perfectly.

You now have a successful model.

You have really done quite well. You also see that C_5 may be about the limit of the system.

So a question is, how do you deal w/ aromatics now? How do you determine the limit of the system? How do you determine the capability of liquids vs gases? You certainly see how it excels w/ gases but how would it work w/ liquids?

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Can you not use your regressions in reverse so that you can estimate tr based upon knowledge of physicochemical properties?

Guess what! You can use the full original model!

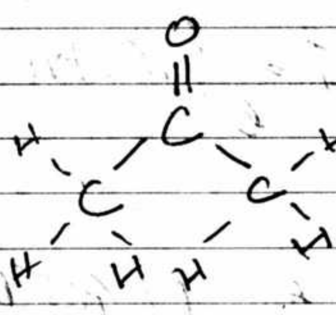
ln(tr) = 2.705E-3 MW + .012 VP + 1.247 DP
- 9.57E-3 T + 2.328

So, it is quite simple to estimate tr.
Let's use water @ T = 150°C
H_2O:
MW = 18 ln(tr) = 4.44
6-66 VP = 99.6 tr = 85.1 min.
9-44 DP = 1.85

I do not think this is the case?

Now use T = 220°C I am not sure.
ln(tr) = 43.5 min.

What about acetone?
@ 220°C



C_3H_6O
MW = 58
VP = 55.7
DP = 2.88

Acetone is throwing a real cog into the model.
Polarity is having a huge effect here.

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Do Not Use This Model Yet

This is Model #6. Remove it.

I would like to add acetone to the model to see how it behaves.

	Species	MW	VP	DP	T	/	tr	ln(tr)
41	Acetone	58	55.7	2.88	220	1	26.49	3.28

Surprisingly, σ is now even lower.

General model is now:

C1 4.739E-3 $\sigma_s^2 = .204$
C2 .012
C3 .781
C4 -9.374E-3
C5 2.275

MW: $tr^* = e^{(.067MW - 5.712E\text{-}3T - 1.501)}$ $\sigma^2_{MW} = 0.48$

VP: $tr^* = e^{(.014VP - 7.753E\text{-}3T + 2.605}$ $\sigma^2_{VP} = 03$

DP: $tr^* = e^{(1.405DP - 5.54E\text{-}3T + 1.209)}$ $\sigma^2_{DP} = .819$

Use Casio Spreadsheet Model GC5

Hold to N = 40 @ this time.

Now predict acetone w/ the adj model n = 41

tr = 26.49		Actual
MW = 90	VS	58
VP = 170		56
DP = 2.35		2.88

So the addition of acetone obviously throws a huge cog into the system.

The general model is

$$\ln(tr) = 4.739E{-3}\,MW + .012\,VP + .781\,DP - 9.374E{-3}\,T + 2.275$$

for acetone

$\ln(tr) = 3.40$

~ tr = 30.12   quite good actually.

what does the general model for water say? @T = 150°C

$\ln(tr) = 3.59$ tr = 36.4 m @ 150°

MW = 18

VP = 99.6   tr @ 220° = 18.9 m @ 220.

DP = 1.85

I think we need to hold off on this model until more information w/ polar materials is evaluated.

So now, hold to the non-polar model tested thru to pentane.

High Polarity seems to throw the model into disarray.

High polarity seems to be anything greater than 0.5.

This seems to be as far as you can go right now.

Questions concern

1. C>5
2. Polar substance

What are the limits of the system and why?

Aug 20 2016 Priest Lake

We are now engaged in general gas chromatography study. Our main book is by Schupp. We found our response table we have been looking for.

To get a weight factor, you solve

$$\frac{\text{Molecular Weight of Compound}}{\text{Thermal response of Compound}} = \frac{W_1}{Th_1}$$

but to compare internally you need to solve

$$\frac{W_1 / Th_1}{W_2 / Th_2}$$

since everything is compared to benzene as the standard to develop the table to begin with.

Let's test the idea:

Water to benzene:

$\dfrac{18/33}{78/100} = .70$ but water is listed as 0.55 to benzene

So this idea DID NOT WORK! Why?

~~Yes, it is~~

First of all, there is a difference in the tabular values for the thermal response of water. One source (Schupp book) has 21 listed. Another source (ESSI Table) has 33 listed.

If you used 21 for water you get

$\dfrac{(18/21)}{(78/100)} = 1.10$

Now I see why! Benzene weight factor is not 1.00, it is .78

OK, I think I have determined the nature of the problem.

The issue is that the thermal response ~~be~~ of 100 has been adopted for benzene, BUT NOT THE WEIGHT FACTOR!

The weight factor for benzene is 0.78 - why?

Because (78gms/mole) / 100 (assumed thermal response)

= 0.78!!! This is actually our reference.

So water to benzene weight ratio =

$\frac{18/21}{.78}$ = 1.10 !! Correct.

Now you have made some real progress. It would be very helpful if you do not lose the Esso table. It is invaluable for analytical work.

It is seeming to me that the thermal response (or weight factor itself) and the dipole moment may actually be the key factors that affect how a compound behaves in a TCD GC column.

		MW	TR	DP	X
Lets look @	Propane	44	64.5	.084	238.4
	Propene	42	64.5	.366	991.5
	Butane	58	85	.132	650.8
	Butene	56	82	.503	2309.8

There needs to be a separation.

	MW	DP	X	
Propane	44	.084	3.70	①
Propene	42	.366	15.37	③
Butane	58	.132	7.66	②
Butene	56	~~82~~ .503	28.17	④

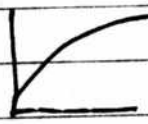
Also not correct.

Maybe thermal response × polarity?

Problem is that for an unknown compound you are not going to have the thermal response available. So that is no good.

It seems like polarity is really important but as it is it skews the model too strongly. Therefore it almost seems like we need to dampen the effect of it, eg $\sqrt{DP}$ instead of DP.

This would curve



which is a good effect.

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You proposed model is now of the form

$$\ln(tr) = C_1 MW + C_2 VP + C_3 DP^{1/3} + C_4 T + C_5$$

This is possible to do.

Let's try this. It should improve matters.

	DP	$DP^{1/3}$
Propane	.084	.438
Propene	.366	.715
Butane	.132	.510
Butene	.503	.795
CO	.11	.479
Pentane	.13	.507
Pentene	.5	.794

The idea has worked perfectly.

You have dramatically reduced the error in the model.

The σ_s^2 used to be ~~[illegible]~~ .205

Now it is .161

Hold to this Model
for Low Polarity

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Our current model (combined) through pentene is now

$$\ln(tr) = 4.864E\text{-}3\,MW + 9.435E\text{-}3\,VP + 1.235\,DP^{1/3} - 9.533E\text{-}3\,T + 1.809$$

and $\sigma_s^2 = 0.161$

or $tr = e^{(C_1 MW + C_2 VP + C_3 DP^{1/3} + C_4 T + C_5)}$

Same MW: $tr^* = e^{(.064MW - 7.513E\text{-}3T - 1.258)}$ $\sigma^2_{MW} = .355$

same VP: $tr^* = e^{(.014VP - 8.863E\text{-}3T + 2.064)}$ $\sigma^2_{VP} = .234$

$DP^{1/3}$: $tr^* = e^{(2.738DP^{1/3} - 8.022E\text{-}3T + .758)}$ $\sigma^2_{DP^{1/3}} = .421$

Now lets reapply to Propane & then Propene

3 vs 6 propane wins! Propane: tr @ 80°C = 4.12m Hair Sample

predict MW = 51 Δ VP = -35 Δ DP = .11 Δ

propane vs actual ① 44 ⑦ ① -42 ⑦ ① .08 (.03) excellent

propene ② 42 ⑨ ② -48 ⑬ ② .37 ㉖

Propene: tr @ 80°C = 5.12m

predict MW = 55 Δ VP = -21 Δ DP = .17 Δ

propene vs actual 42 ⑬ ② -48 27 ② .37 .20 ② Σ=4

propane 44 ⑪ ① -42 21 ① .08 .09 ① Σ=3

The model did not successfully identify propene but it did correctly identify propane. But you can see it is close.

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The model is doing much better now. It has zeroed in considerably and you can definitely zero in on the target components.

Let's look @ CO:
tr = 4.27 @ 80°C

WM Predicted properties are

	MW	Δ	VP	Δ	DP	Δ	
	51		-35		.12		
Actual	28	23 ②	-192	157 ②	.11	.01 ①	Σ=5
Propane	44	7 ①	-42	7 ①	.08	.04 ②	Σ=4

So it does not identify CO correctly but it is trying. It appears that the polarity should be given more weight than it is.

We believe the weight factor should now be

~~MW $2/\sigma^2_{MW}$~~

~~VP $1/\sigma^2_{VP}$~~

~~DP $3/\sigma^2_{DP}$~~

and this has been incorporated into the spreadsheet.

This means that you must bring this into the ranking system.

I think that these weights should still hold.

Don't do this yet.

This means that you must adjust the ranking to:

CO: $2(2) \; \frac{+\,1(2)}{6} \; + 3(1) = 1.5$

Propane $2(1) \; \frac{+1(1)}{6} \; + 3(2) = 1.5$

This means that they tie out (the lowest number will still win)

Rank	Wgts	
1	3	3
2	2	4
3	1	3
		$\Sigma = 10$

Propene Comparison from previous page

propene $[2(2) + (1)2 + 3(2)] \div 6 = 2.0$

propane $2(1) + (1)1 + 3(1) / 6 = 1.0$

Propane still falsely wins here so I am not sure there is any real advantage.

You should probably just stick to the original plan. If there is a difference of only 1 however, it is probably way too close to call.

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Now the question is what happens when you bring something like acetone back into the picture?

Acetone Data is

	Species	MW	VP	DP	$DP^{1/3}$	T	1	t_r	$\ln(t_r)$
41	Acetone	58	55.7	2.88	$\boxed{1.42}$	220	1	26.49	3.28

The results of this addition are

~~C_1 3.626 E-4~~ ~~$\sigma_s^2 = 0.175$~~

~~C_2 9.825 E-3~~

~~C_3 1.497~~

~~C_4 −9.228 E-3~~

~~C_5 1.931~~

Now

~~MW & VP~~

Do not use this model. Page 45

~~MW: $t_r^* = e^{(.067MW - 5.712E\text{-}3T - 1.501)}$ $\sigma^2_{MW} = 0.48$~~

~~VP: $t_r^* = e^{(.014VP - 7.153T + 2.605)}$ $\sigma^2_{VP} = 0.30$~~

~~These are indeed the same as previously achieved. but now for $DP^{1/3}$ w/ acetone added:~~

~~$DP^{1/3}$: $t_r^* = e^{(2.822DP^{1/3} - 7.906E\text{-}3 + .725)}$ $\sigma^2_{DP^{1/3}} = .413$~~

Here is what you are seeing.

1. The model for MW & VP is working fairly well up to the pentane level before you put in acetone.

2. The model for acetone is working only for the polar solutes.

The conclusion they reached is that you require a polar model and a non polar model.

If it is an unknown you can not really even tell.

It appears that our model for Polarity less than 0.5 is valid and accurate up to the pentane level.

If Polarity is high it seems like we need to develop a high polarity model alone

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We now have a HIGH POLARITY & ($n=25$)
a LOW POLARITY model ($n=40$)

The Low Polarity Model is as we had before acetone was added:

C_1 4.864E-3 (MW)
C_2 9.435E-3 (VP)
C_3 1.235 ($DP^{1/3}$)
C_4 -9.533E-3 (T)
C_5 1.809 (C_0)

and $\sigma_s^2 = 0.161$

($DP \leq 0.5$)

The HIGH Polarity model ~~($DP \geq 0$)~~ ($DP \geq .5$)
is

with input data of $DP \neq 0$

C_1 0.02
C_2 1.175E-3
C_3 2.431
C_4 -.011
C_5 0.424

$\sigma_s^2 = 0.142$

These now seem like respectable models. Now they can, in a practical sense, only be used w/ one variable @ a time.

Therefore we must separate the variables from each model

$$\ln(t_r) = C_1 MW + C_2 VP + C_3 DP^{1/3} + C_4 T + C_5$$

$n=40$ Low Polarity Model $(DP \leq 0.5)$

See Previous Page for C_i Values

MW: $t_r^{*\sim} = e^{(.064 MW - 7.513E\text{-}3 T - 1.258)}$ $\sigma^2_{MW} = .355$

VP: $t_r^{*\sim} = e^{(.014 VP - 8.863E\text{-}3 T + 2.64)}$ $\sigma^2_{VP} = .234$

$DP^{1/3}$: $t_r^{\sim} = e^{(2.738 DP^{1/3} - 8.022E\text{-}3 T + 0.758)}$ $\sigma^2_{DP^{1/3}} = .421$

$\ln(t_r) = C_1 MW + C_2 VP + C_3 DP^{1/3} + C_4 T + C_5$

Look Ahead

n=25 High Polarity Model ($DP \geq 0.5$)

See Previous Page(s) for C_i values:

MW: $t_r^* \approx e^{(.035MW - 1.221E-3T + 0.526)}$ $\sigma^2_{MW} = .357$

VP: $t_r^* \approx e^{(8.844E-3VP - 8.016E-3T + 2.65)}$ $\sigma^2_{VP} = 0.33$

$DP^{1/3}$: $t_r \approx e^{(2.756DP^{1/3} - .011T + 1.195)}$ $\sigma^2_{DP^{1/3}} = 0.198$

This model does not seem to be working @ all. for acetone

DP = 2.00 T = 220 t_r = 14.80 min. sounds reasonable

This model does not seem to work. MW & VP estimates are way off for acetone.

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The Low Polarity Model seems to work fairly well up to and including pentane.

The High Polarity model has some real problems to it

Maybe w/ more data the High Polarity model will start to work better.
You actually only have one data point w/ DP ≥ .5 for acetone so that does not speak very well.

Let's use data w/ DP only ≥ 0.5

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Revised High Polarity Model with $DP \geq 0.5$
Data Only $N=16$

C_1 −.077
C_2 .036
C_3 .841
C_4 −.012
C_5 7.097

$\sigma_S^2 = .099$

Notice the high constant.
This seems about right.

$$MW: \quad tr^* = e^{(.028MW - 6.952E-3T + .981)} \qquad \sigma_{MW}^2 = .505$$

$$VP: \quad tr^* = e^{(.018VP - 8.403E-3T + 2.823)} \qquad \sigma_{VP}^2 = .301$$

$$DP^{1/3} \quad tr^* = e^{(2.534DP^{1/3} - .012T + 1.554)} \qquad \sigma_{DP^{1/3}}^2 = .285$$

This model really is not working very well.

The idea of the individual Contributions is not working very well.

$MW = 136$
$VP = 130$
$DP = 5.2$

Now sub into full model

$\hat{tr} = 1.13$ min.
not very good. 15 rt.

Wait a minute. Our model works extremely well for the actual value of Acetone.

Including

MW

VP

$DP^{1/3}$

T^{o}

and a Constant

It is essentially perfect.

This means the individual regressions are causing a problem of some kind. Why?

For some reason it seems like you need to add all the components of each regression to get a first estimate.

But why would this be in this case but not the low polarity model. This make no sense

-The DP portion of the model seems to be coming up w/ the whole contribution. Why?

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With the polar model, the DP portion is capturing only a small portion of the signal. Actually about 1/2 of the total.

So why is the Low Polarity Model capturing the signal fairly evenly?

Maybe because the DP relationship is highly non-linear. Maybe because the behavior of the column is highly non-linear.

So what if you use the low polarity model for ~~VP &~~ , MW & DP.

and then use the high polarity model for DP ~~estimate~~ only.

Our first estimates for the low polarity model are for acetone @ 220 ($t_r \approx 26.5$ min)

MW	97		58	
VP	190	vs	55.1	
DP	4	actual	2.88	No idea why

If we plug these into the high polarity ~~model~~ model we get $t_r = 0.14$ min.
So obviously something completely overwhelms the system.

But maybe the ratios are close

There is a question of iteration.
Can it work?

A decent high polarity combination model is,
for $DP \geq 05$

$\ln(tr) = -.077\,MW + .036\,VP + .841\,DP - .012T + 7.097$

Assume $DP = 2.88$ need $\ln(tr) = 2.88$
$T = 220$
then

$\ln(tr) = -.077\,MW + .036\,VP + 2.42 - 2.64 + 7.097$

$\ln(tr) = -.077\,MW + .036\,VP - 0.22 + 7.097$

$\ln(tr) = -.077\,MW + .036\,VP + 6.877$

What if we accept MW + VP
from the non polar ~~mod~~ model?

What if we accept $\ln(tr)$ from the $DP^{1/3}$ High Polarity model

$\hat{tr} = e^{(2.756\,DP^{1/3} - .011T + 1.195)}$

$\hat{tr} =$ ~~6~~ 14.80 so this is first estimate for tr. $\ln(14.80) = 2.69$

So now we have

$2.69 \overset{\sim}{=} -.077\,MW + .036\,VP + 6.877$

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or $0.077MW = .036VP + 4.187$

or

$$MW = \frac{.036VP + 4.187}{.077} \text{ or}$$

$MW = 0.47 VP + 54.4$

or

$\hat{\ln}(tr) = (-.077)(.47VP + 54.4) + .036VP + 6.877$

or

$\hat{\ln}(tr) = -.036VP - 4.19 + .036VP + 6.877$

or

$\hat{\ln}(tr) = 2.69$ So this is circular logic.

Ok let's rethink this process

1. Come up w/ 1st estimates w/ linear models
2. Plug back into comprehensive model.
3. Or could go back into individual model & get new estimates.

Example: 1st estimates for High Polarity model w/ Acetone.

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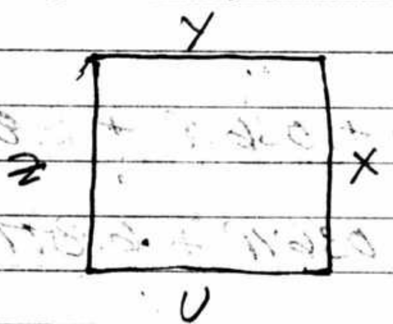
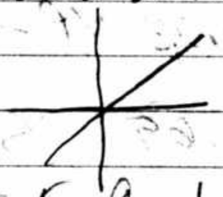
My assessment is that non-linear behavior of the column is causing a failure of the High Polarity Model attempt.

Right now I am not sure of anything that can be done



X Y Z U
2, 4, 8, 3

Multidimensional plotting



5, 9, 1, 4
8, 2, 2, 2
1, 3, 6, 8 ...

It is proposed that

$\ln(tr) = \frac{K}{T} + C$ instead of $K \cdot T$

but $\frac{K}{T}$ let $K=5$ then $\frac{K}{T} = \frac{5}{T}$

is there a number such that $C \cdot T = \frac{5}{T}$?
yes. $C = \frac{5}{T2}$

$C = \frac{T}{2.5} = \frac{2}{25} = .80$

$\ln(tr) = \frac{5}{T}$ let $T=2$

$\ln(tr) = 2.5$ $\ln(tr) = 2.5 = C \cdot T$

This is an interesting problem.
One person proposes that

$\ln(tr) = \frac{K}{T}$ Another proposes $\ln(tr) = C \cdot T$

Can they both find an eq. solution
but neither is this linear.

$\ln(tr) = \frac{K}{T} = C \cdot T$ then $C = \frac{K}{T2}$ but this is not linear.

Example. let $K=2$, $T=5$ but they are both

$\ln(tr) = \frac{2}{5} = 0.4$ but $C = \frac{2}{25}$ linear in K & C.

and $C \cdot T = \frac{2}{25} \cdot 5 = \frac{2}{5} = 0.4$

Which is equivalent. Therefore there is a C that can be found that satisfies the condition.

for the first case, $K=2$
In the second case $C = 2/25$
and in both cases $\ln(tr) = \underline{0.4}$

So there is no need to plot K/T

$y = \frac{K}{T}$ $y = KT$

This is not a line. This is a line

This suggests that your model should have been changed to

$$\ln(t_r) = C_1 \cdot MW + C_2 \cdot (VP) + C_3 DP^{1/3} + C_4 \cdot \left(\frac{1}{T^\circ}\right) + C_5$$

We should try ~~this~~.

I am not seeing any advantage to this model change.

σ_s^2 is larger, ie 0.261 vs 0.161

So your problem is that you have built a decent model but you don't exactly know how to use it except for breaking it into parts that do not work as well as the original.

Lets work w/ the Low Polarity Model

Assume $t = 10.2$ min @ 150°C

First estimates:

MW 73.5
VP 72
DV 1.03

However, the full evaluation is now helpful as it tells how the full model evaluates. It comes in @ 14.6 min even though each individual component comes in @ 10.2 min. Therefore we know that it is too high by a ratio of approx $\frac{14.6}{10.2} = 1.43$

Or, we consider reducing by .70. So

$MW \cong 73.5\,(.7) = 51.5$
$VP \cong 72\,(.7) = 50$
$DP \cong 1.03\,(.7) = .72$

Now we look @ candidates
Our closest match is definitely butene with
MW = 56.1 | Full Evaluation
VP = ~~117.2~~ -6.6 | This evaluates to | but actual
DP = .503 | 8.70m | is 2.65m.

This is definitely our closest match, so this worked very well.

The model seems to work very well w/ low polarity materials.

However, the weighted avg is 3.94 which is much closer than the full evaluation. The full evaluation is actually very poor.

So here is a Case where it Come out the opposite for this Case the individual regressions did very well but the full evaluation did poorly. Why is this?

Actual t_r = 10.2 min mean.

What we see is that we have no measured data that matched this type of value. So it never would have occurred yet & it would consequently be a new Compound.

What would have worked is 60°C.
Rework @ 60°C @ 10.2 min
MW = 65.5
VP = 28
DP = .52

Butane & Butene are definitely the candidates.

	MW	Δ	VP	Δ	DP	Δ	t_r	Δ
Butane	58.1	①	-.8	①	.132	②	9.6	①
Butene	56.1	②	-6.6	②	.503	①	13.0	②

- The answer is definitely butane Σ = 5 vs Σ 7

Now we input actual value into the full evaluator. We get 12^{3} min.
This is acceptable as a Confirmation.
Butene actual value come out w a full evaluator of 17^{m} which is a bit high.

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Lesson: Both butane & butane remain candidate but butane is the stronger of the 2 candidates.

Now if you can get this much activity on 40 min @ 80° you should be able to bring quite a bit more into the column @ 150°C.

For example, hexane, heptane, etc probably up to octane but you do not have any of this.

But you have gasolene!!!
You could put gasolene into the column & white gas or coleman fuel would be a great experement.

It looks like naptha could also go in.
Xylene should be able to go in.

Octane
naptha
Xylene

Ketones tail a lot. (acetone)
Alcohols tail a lot

Acetates & ether I know nothing about.

April Aug 21 2016 Priest Lake

The lower polarity model seems to be doing a pretty decent job. I anticipate that I can extend it to octane, naptha, and xylene upon return.

You see that you are interested in extending to ketones, acetates and ethers but you do not know what these are.

Varian lists the following type of compounds that can be separated on a GC.
Alcohols Aldehydes Amides Polar Substituted
Carboxylic Acids Esters Aromatic Hydrocarbons
Ethers Heterocycles, Halogenated HC'S
Ketones, Nitriles, Nitroalkane Aromatic
Phosphonates Sulfides

Actual graphs are:
Alcohols Aldehydes Carboxylic Acids
Esters (Amyl Acetate), (Butyl Acetate)
(Ethyl Acetate), (Propyl Acetate)
Ethers
Ketones

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The solvent package from Flinn Scientific includes: $54 + Shipping

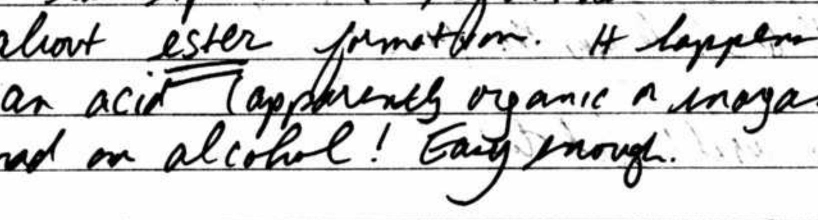
Two Alcohols
Three Esters
Four Ketones

GC is $2K

Methyl Alcohol
Ethyl Alcohol
Acetone
MEK
Methyl Isobutyl Ketone
Pentanone
Ethyl Acetate
Propyl Acetate
Butyl Acetate

The lab experiment (GC) from Vernier talks about ester formation. It happens between an acid (apparently organic or inorganic) and an alcohol! Easy enough.

Example: methyl alcohol (ie, methanol) + acetic acid (glacial acetic acid, or maybe even vinegar) produces methyl acetate (which apparently is an ester).



Ketone — Carboxylic Acid — Ester — Ether

This is the root of the carbonyl crowd

(this is the real root of the organ crowd)

Projects:

Ok, now we know more about
ketones, esters & ethers.
We also know why they are all polar to some
degree because they have oxygen involved
in all cases.

Also we have studied the physical properties
section of Crippen's book. This is very insightful
and you are definitely on the right track.

One of the problems with your highly polar model
is that you actually only really have one
data point w/ acetone and it is a highly
tailing peak. I think that you need the
Porapak Q like you thought.

Today we would like to:

1. Look @ polar chromatograms more closely
& ask if we should be working on a polar
model yet. Probably not.

2. Consider posting the VC response

3. How do you make an ester suitable for GC?
Do you need to? When would you find an
ester? What about derivatives in general?

4. We have ham study

5. We have our Biology kit - No we don't!

6. We have Palmsens w/us - Impedance?

7. We have our Chemistry kit & Chemlab Software

8. We have our antenna analyzer and all that entails w/ ham study & Palmsens impedance.

9. We have lots of magazines & ham catalogs

10. We have some good statistics work

These are the project opportunities.

We do understand weight factors now also.

Physical Chemical Properties - In the Field.

1. BP - MP - Freezing Point

* Boiling Point: For Liquids
* Melting Point: For Some Solids

Freezing Point: Not possible

* 2. Index of Refraction (for liquids)

* 3. Density

4. Optical Rotation

5. Molecular Weight

6. Conductivity, TDS, pH

7. Electrochemistry

GC High Polarity

We do have another data point.

Water @ 220°C t_r = 4.26m front end of peak.
MW =
VP =
DP =

HEPA Filter Sample

First Examination

1. Microscope not sufficent.
2. HEPA is in 3 layers; dark backing can be removed.
3. Blank water TDS is 40-45.
   Filter sample added, room temp. TDS climbs to 66-65.
4. pH of blank is 7.0
   pH of sample is 7.0

Now add 1 drop of 01M HCl to solution
TDS rises to 99!

Refractometer is set to zero with blank H_2O.
Sample Brix is also 0.0

pH of blank is 7.0
pH of sample is 7.0
pH of acidic blank (1 drop 0.1M H_2O) is 4.0
pH of acidic sample is 3.4

TDS of sample after 1 drop 0.1 M HCl has risen to 283. This is a significant rise so acid has a significant affect upon the sample. Total TDS affect ≅
283 - 99 = 184

This is significant.

We know now that acidification of the HEPA sample is having a significant effect upon the sample.

This suggests that electrochemistry can be applied. We may be able to determine inorganics

Now to test sample (new) w NaOH.

TDS of ~~samp~~ blank is 43 PPM.
TDS of sample in H_2O alone rises to 57.

TDS of blank (H_2O) w/ 1 drop 0.1M NaOH is 64. (Does not rise as high as acid, which rose to 99).

TDS of sample in H_2O w/ 1 drop 0.1M NaOH is only @ 68. So no significant effect seen.

Conclusion: Acidification has a marked impact upon the sample. Alkalinizing does not show such an effect.

The sample is the thinnest layer of the HEPA filter, the most transparent. The HEPA filter consists of 3 layers

Next we test the dark layer of the filter. It did not have any real impact at all.

You need to be careful that you are not dealing w/ an additive effect since there are 3 layers in the HEPA filter.

You need to work w/ a blank filter as a control.

A 2nd sample w/ 2 layers (only the backing removed) does not seem to have the effect either that the first sample did.

Remember that acidification alone produced a TOS of 99. Now with 2nd sample & 2 layer addition w/ HCl we only get a TOS of 103. So no significant effect here? /??

Heating the water had some effect but not large. Nothing has duplicated the first sample. We will consider microwave also.

You are seeing that you are fairly limited in what you can do. You only learn that acid appears to have some effect upon the sample and that
* at least a portion of the sample is soluble.

I do not know why such a big difference between samples.

Actually, there does appear to be some effect from the acid, but it is not what you think.

The blank w/ H_2O & <u>2 drops</u> 0.1M HCl reaches 260PPM.

But the sample w/ 2 drops HCl is only ~~130~~. ~~140~~. 135
So the sample might be neutralizing the acid. This would mean the OH is being released when the acid is added.

Repeat this test.
Blank: H_2O w/ 2 drops HCl ⇒ TDS: 205
w/ Sample added: —

Ok the next thing that we learn, which we were anticipating, is that gasoline makes a very good solvent.
We have immediately removed the material from the filter. Use a clean filter as a blank and you are all set.

This means that the materials are primarily non-polar.

You have learned how important and fluvious gasoline is as a solvent

Octane! We will head towards the GC with it and see how we do.

Aug 25 2016 Pruet Lake Continues

[redacted]

[redacted]

5. Multiple linear regression capability w/ Mathcad using arbitrary basis functions is a very powerful tool. We need to exploit this function along w/ plotting capability & programming capability.

6. You have a score of projects that you are not getting to yet.
    1. Ham Study
    2. Impedance study
    3. Palmsens impedance study
    4. Fuel cell project, w/ impedance & voltammetry no less.

But POWER IS indeed a problem and limitation on many of these, including
1. Mathcad
2. Palmsens
5. All of your magazines.
6. Arranging w/ Vernier

We will not have power most of the time @ Camp except when we are in N.M. Better plan the work with no power.

7. Physiochemical properties capability.

(1) BP	(2) MP
Beaker	Melt Block
Oil	Stove
Theronometer	Mag. Glass

A distillation setup is a very nice way of working with the boiling points.

(3) Index of refraction (liquids only)
(4) Density
5. Conductivity, TDS, PH

8. Your GC models can be much more easily explored now w/ Mathcad capability. (Need power though)

9. HEPA filter sample is coming up.
10. You have learned a great deal about hair breakdown now with conc. NaOH & (or KOH) and microwave. This has many application to the env. filament project.

✓ 11. UC response has been posted.

12. We are learning about ketones, esters and ethers. Also how they are introduced into GC.

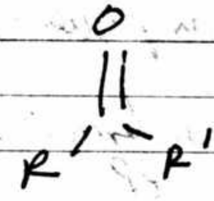
Ethers (Either)
r

Carbonyls:
Ketones deprimary carbonyl
Carboxylic Acids
Ester

This is an important step in organic chemistry.
On ketone, Carboxylic acids, esters and ether

$R-O-R'$

Ether!
the simplest of
the group!

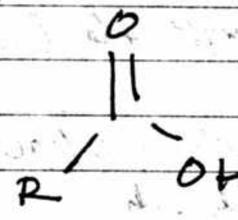


Ketone - the root of the
carbonyls!

Now we ~~start~~ substituting.

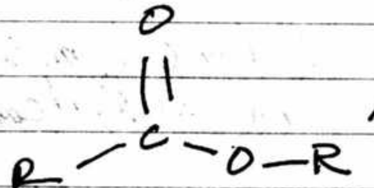
So what we learn here
(ie, OXYGEN FUNCTIONAL GROUPS)
is that it all starts with
an ether, an an ~~ether~~
ether ~~starts~~ with an O
and either we have
a single O or a double O.

substitute
an OH



Carboxylic Acid

substitute
an O



Ester

Double O's are carbonyl
& the start of the carbonyl
IS THE KETONE.

From the ketone,
We go to the Carboxylic Acid
and then we lead to an ester, which interestingly
enough combines both a double O and a
single O.

We are going to make an ester soon.

I realize now that you cannot use Mathcad linfit() for the GC model. Exponential harmonics are only a function of one variable, x. GC model is a function of several variables, ie it is a multi-variate linear regression model.
I am not sure what it take for MCAD to handle that problem. In the meantime GC models remain as is.

The book I have is not complete enough to describe a multi variate linear regression model.

—

We do have a lot of magazines. Is there a day to catch up on the magazines?

13. You are also working out your antenna situation.
14. MFJ radio should be sent in.

—

You make an ester by:

1. Mix a carboxylic acid & alcohol warmed up with a few drops of conc. sulphuric acid.
2. Apparently you need to distill it to capture it but since you smell it you can capture the gas!

Easy to find an ester on ebay

Conclusions:

1. Vernier UV purchase is not cost efficient relative to full size machine.

2. GC Vernier is also expensive relative to the capability in the field. Attractive but also expensive.

3 ~~If~~ Is there an inexpensive portable UV light source?

4. You can take the Thermo VIS-NIR with you at no cost. What you do not get w/ this is Fiber optic & UV sensor capability And a bigger package that requires AC power.

5. You have decided that fundamental physical properties of
   1. Melting & Boiling Points   Optical Rotation.
   2. Index of Refraction
   3. Density

are of great interest to you, but the material must already be separated and pure. This seldom exists.

6. Field deployable melting point methods have been proposed.
   Sardine, Sand, Stove, digital thermometer.

Scenario #4 is to take & use your existing VIS – & NIR Thermo Scientific

This will save you $1000 and still give you some organic capacity. You know the system and it is not too heavy

Another option is to buy an inexpensive UV instrument for $1200. w/ no logging software. Single wavelength. It will require AC power and will have some weight to it.

This really is not an attractive option.

So now we have four scenarios

Factors are
1. Enhancement to Field Capabilities
2. Enhancement to Lab Capability
3. Cost
4. Weight Relative to Location of Use!
5. Size Relative to Location of Use!
6. Longevity + Durability
7. Timing
8. Shipping Convenience

Scenario 1

$ 3325 Vernier VIS + 3 Sensors
Vernier GC
Logger software
Column, BSA, Syringe

~~Good~~ field capability,
expensive, no lab enhancement
Ships to NM in Oct

Scenario 2

UV fullsize $ 2205
Column BSA

No portable
equipment

Modest Lab Enhancement
Ships in Spring 2017

Scenario 3

Vernier VIS + 3 Sensors
$ 3275 Logger Software
Column, BSA

UV Full Size

Split Shipment
Wallace now
+ Wallace later

Scenario 4

Take VIS-& NIR
Buy UV OR GC Vernier 2K
a b

Full Size UV in Spring? 2K
BSA now 75
Take methanol
Logger 350
$ ~4500

[redacted]

Scenario 5

$ 4500 Vernier all the way.
GC, UV-VIS
Logger
$ 4500
Ships to NM only
No Lab Enhancement
$ 4500

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In the field head fr.

1. Analyze of data collected in summer with
    1. Infrared
    2. GC
    3. UV in future
    4. Microscope - High level

2. In field
    1. Analyze Infrared
    2. Analyze GC
    3. Electrochemistry Galore
    4. Physiochemical operations
        1. Melting Point
        2. IOR (Liquids only)
        3. Density
        4. pH
        5. σ, TOS
        6. ORP
        7. Possible some melting point & boiling point.
        8. % Carbon

yes! 5. What about Polarimetry?

yes! 6. VIS - σ, NIR work

yes! 7. TLC !!!!

→ It looks like we need some iodine crystals & Conc. sulf. acid in a spray bottle.

8. Microscope - Low Quality Work
9. Oscilloscope
10. "Rice Machine".

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Winter Travel Plans

Travel Inventory Considerations

CRC Book?
10R - Refractometer
Melting Block, magnifying glass
Scale
Digital Thermometer
6 in 1 meter
Palmsens
shotglasses, custom tubes, holder, electrodes, cases, Manual
Electrochemistry Book.
IR Book (2?)
Laboratory Techniques Book
~~VIS - IR spectrometer~~
Test Tubes, beakers, Stirrers, needle, meas. spoon, Scoopula
Chemicals
Water Bottle
Portable pH meters
USB Microscope
Chemistry Micro kit
TLC plates, jar, solvents?
Need IR Flash Drive & Software?
Need Big laptop, Netbook, Tablet, Phone
Chem Book
Syringe(s) big & small
Metal Weigh Boats, Plastic Weigh Boats
Water glasses
Regular Torch?
Mapp Torch
Pipette & Stems
Capillary Tubes
Picoscope & Electrodes

Need Calculator
N All Chargers
N FRS Radios
Transistor Radio !?!
CRC VP Tables!..
Chemical Set
Torch & Calorimeter & Cups & washers
Melting Blocks
Thermometers
Tongs
Refractometer
Polarimeter

Reg Pipettes
Filter Paper
Iodine
Antenna Analyzer
Permanent Marker
"Rife" Machine
Glass Slides
& Cover Slips
amino acids
Solvents

Ham books, Exam,
Logbooks, Atlas

Lowe's.
1. Mapp Gass Torch
2. Tubing
3. Cell Phone Case
4. Pens

Winter Travel Plans ☆

Need iodine crystals
Nebulize w/ sulfuric acid.
TLC book?
GC Book
Math Book - Mathcad?
Biology Book
CDB- Protein -Lipid Samples.
Random Samples, Milk; Oil, Sugar
Water Pollution Lab Papers
HEPA filter material
Blood Poker, Dual in Pipette; Microtips, Electrophoresis
Chemicals - in kill set

Acetone	Dist Water
Methanol	Baking Soda
90% Isopropanol	Mineral Oil
Xylene	Washing Soda
Ether	Sugar, Salt
Ester (Acetate)	NaOH
MEK	KOH
Micro Set Chemicals	Naptha?
H_2O_2	White Gas?

H_2SO_4
Iron Detection
HCl
HNO_3
Ammonia
Vinegar
$FeSO_4$ - Powder & Solution
Fe 3
TiO2 Al
Mn Co

I have coming

Rec. 1. Ether
Rec 2. Ester (Acetate)
Rec 3. TC Plates (50)
Rec 4. 6 in 1 meter
Rec 5. UV Light
Rec 6. Melting Pt Block Shipped
Rec 7. .01 gm Scale
Rec 8. Iodine
Rec ~~9. Polarimeter~~
Ebay & Amazon & Joy Lay
Rec 10. Phosphate
Remove -- Pool Supply
Rec 11. [redacted]
(1) Rec (2) Rec ~~12. TLC Books TLC~~
Rec 13. Small Test tubes

Need
1. Mapp Gas - Torch
~~2. Iodine Crystals~~
3. H_2SO_4 - nebulizer

Rec 14 Med Test Tubes
Rec 15 Large Test Tubes
Rec Chromatography Paper
Rec Spare Polarimeter Sample Tube
UPS! Reflectance Spectrometer
Paper Chromo & Electrophoresis Books

Aug 28 2016 Road Trip Planning

I have studied polarimetry at an introductory level And it promises to be interesting, beneficial and promising & beneficial. I have a Immanual Kelson coming.

[redacted]

1. Chemicals
   Ester, Ether & Iodine

2. Melting point improvement.

3. TLC Means — UV
   - a new field of study. — Plates
   it should be powerful. — Iodine

4. Full Scale pH, σ, ORP, TDS

5. Polaremeter

6. Digital Scale

What I would like to do now is to make two investigation w.r.t. the GC model.

1. Linear regression capability of Mathcad - you can't use this w/ multivariable
2. Explore using t_r vs $\log(t_r)$
3. Also looking @ plot of residuals would be helpful.
4. Magazines would be good for today also.

We find that there is no distinct advantage to using $\ln(t_r)$ vs just using t_r.
Our σ_s = 1.9 min which is quite reasonable.

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Therefore our modified model using tr instead of ln(tr) is

MW	C_1	0.071
VP	C_2	9.144E-3
$OP^{1/3}$	C_3	4.393
T	C_4	-.031
Ca	C_5	2.837

$\sigma_S = 1.9$ min (not σ_S^2).

Now let's go for individual regression:
No longer ln(tr) but tr direct

(0.17) Found an error.

$\tilde{t}_r = .017\,MW - .027T - 1.225 \qquad \sigma_S = 2.2$ min

$\tilde{t}_r = .034\,VP - .029T + 8.819 \qquad \sigma_S = 22$ min

$\tilde{t}_r = 7.518\,OP^{1/3} - .029T + 4.049 \qquad \sigma_S = 2.2$ m

This shows a substantial improvement in the general model, using tr instead of ln(tr).

The error is now very evenly distributed.
Let's put out cases and test some cases.

There is no exponential any more, only linear forms except for OP.

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We also would like to change the vapor pressure values.

We are getting extremely stable values now between the weighted avg of the individual regressions vs the full multivariate model.

This is excellent. We do not seem to need to change the vapor pressure values, however when you lose the CRC handbook you will be at a serious disadvantage.

You will be forced to construct a new model based on different tabulated VP values, i.e. from WebMO and ChemSpider.

This should be doable but if you xerox the CRC you should also be OK.

Let's test the model out. It is only for low polarity items. Random testing.

Do not do this.

150° $t_r = 1.24$

We get MW ≅ 38.5 ~~(1.33) = 51.2~~

VP ≅ -95 ~~(.75) = -71~~

DP ≅ .008 ~~(1.33) = .01~~

Now the weighted avg is 1.24 min

But the full evaluation is 0.93 min

So we can adjust by ~~1.24/.93~~ = 1.33

.93/1.24 = .75

This candidate could be one of several.
It is obviously much better to have them done
@ 80°C vs 150°C to get a better separation

Candidate propose MW = 38.5 VP = -95 DP = .008

Σ			MW	Δ	VP	Δ		DP	Δ	
6	Propane	①	44.1	5.6	-42.3	53	③	.084	.076	②
4	Ethane	②	30.1	8.4	-89	6	①	0	.008	①
4	CO_2	①	44.0	5.5	-79	16	②	0	.008	①

Most likely candidate appear to be ethane or CO_2 but we actually tentatively identify as propane

The evaluation must be made @ 80°C, not 150°C.

At 80°C our candidate is t = 4.12m
We have a wgt. avg of tr = 4.10 min
and a full evaluation @ tr = 4.21 min
Very good here.

Our physical properties are:
MW ≅ 44 Propane or CO_2.
VP ≅ -70 Reasonably Volatile
DP ≅ .03 very Slightly polar

Now our evaluation leads to:

Proposed Weights 3 1 1

				MW (Δ)		VP (Δ)		DP (Δ)
1.6	6	Propane	3 ①	.01	③	28	②	.05
1.8	5	Ethane	3 ②	14	②	19	①	.03
1.0	3	CO_2	3 ①	0	①	9	①	.03

This leads to our strongest candidate as CO_2
But we also believe this to be highly questionable.

This suggests that we really need to consider reweighting the data. We know that VP is subject to a lot of error and DP is highly sensitive.
You seem to have some problem here.

We can see from inspection that closest by MW certainly appear to be propane & CO_2. We also see that CO_2 comes out before propane by VP and also because of the DP.

Therefore propane is the logical choice, but how do we get there?

First by MW: Top candidates are Propane & CO_2.
By VP, CO_2 elutes before Propane.
By DP, CO_2 elutes before Propane.
Since we have a high tall peak already of CO_2 we conclude that it is propane.

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We can see that the molecular wgt in both Cases is very close. VP & DP relative ranks are good also but absolute values are not so reliable.

This suggests molecular weight has numerical value & VP & DP have rank value.

Now let's look @ Propene @ 60°C t = 5.12 min
We get a Combined avg of 5.32 min

Our values are therefore

ln(VP)? Consider using actual VP

	tr (meas)	tr (calc)	MW	VP	DP
Ethane	1.36	1.23	30 28	-90 -151	0 0
Propane	4.12	4.15	44 44	-42 -70	.08 .03
Propene	5.12	5.32	42 50	-48 -40	.31 .09

True Ranking of MW: (Propane ≅ Propene) > Ethane

True VP: Ethane < (Propane ≅ Propene)

True DP Ethane < Propane < Propene

This clearly is a valuable model. You can easily discern between these three materials.

You also know that on average
each C will have about 2 H.s

So, if it is a hydrocarbon, it should
have a MW of approx

Aliphatic Hydrocarbon MW ≅ $n(12) + 2n$ where $n = 1, 2, 3$ etc

eg

	~MW	Calc
n = 1	14	
2	28	~~28~~ 30
3	42	~~44~~ 44, 42
4	56	~~50~~
5	70	
6	84	

If it does not match the above, it most likely is not a hydrocarbon.

Vapor Pressure Tally:

	VP (ChemSpider)	BP	TC
Methane	205286 mm Hg	-164	760mm = 1 atm
Ethane	28842	-89	
Ethene	35.04	-104	
Propane	7271	-44	
Propene	8471	-48	
Butane	1558	-1.0	
Butene	37	-6	
~~Propane~~ Pentane	420	36	
~~Propene~~Pentene	10	30	
O_2	321621	-183	
N_2	431351	-196	
CO_2	56	-88	
CO	0	-313	
H_2		!! 440 ~~400~~ °C - ??!!	

We can already see that
vapor pressure is very problematic.

We can see that w/ the exception of CO & H
things work pretty well.
Let's use it instead of vapor pressure.

It makes me wonder if I should use
thermoconductivity.

What we are learning is that CO & H_2 throw
everything for a huge loop. They truly are problematic.
You need properties that are easily accessible.
Even dipole moment is questionable.

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Notice that VP temperature worked really well for the gases, including H_2 & CO.

This says that your model is good the way that it is but that you must have the CRC data with you to extend the model further.

Let's look @ how many pages are involved in the CRC book.
14 double pgs for VP.

Let's just leave the model alone.

Let's continue and apply the model to butane
$t_r = 9.51$ @ $T = 80°C$

We get a combined avg t_r of 10.3 min.
(a little on the high side but quite good still)

This proposes the following

MW ≃ 76
VP ≃ 90
OP ≃ 1.1

This places the candidate @ the pentane level
But this is wrong. It is actually <u>butane</u>

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[illegible] Evaluation is 11.11 but actual is 9.57

$\frac{9.57}{11.11} = .86$

We had $MW = 76 \Rightarrow 65$

$VP = 90 \Rightarrow 77$

$DP = 1.1 \Rightarrow .84$

$\frac{11.11}{9.57} = 1.16$

Now reset to these values. This leads to a combo mean of 9.19 now 2nd iteration

$\frac{9.57}{9.19} = 1.04$

$MW\ 65 \Rightarrow 68$

$VP\ 77 \Rightarrow 80$

$DP\ .84 \Rightarrow .87$

leads to a new mean of 9.45 min. This is reasonable.

But this still leads to a $\underline{\underline{C_5}}$ which is not reasonable.

It makes me think that we should adopt a expression of

$$C_1 MW + C_2 VP + C_3 DP^{1/3} + C_4 T + C_5 = C_6 t_r^{b}$$

Now you can divide everything by C_6 and so lead to

$$C_1 MW + C_2 VP + C_3 DP^{1/3} + C_4 T + C_5 = t_r^{b}$$

So this is equivalent to

$$C_1 MW + C_2 VP + C_3 DP^{1/3} + C_4 T + C_5 = t_r^{C_6}$$

if we have

~~$y=ax^b$~~ $y = x^b$

$y = 3^5$ $y = 3^6$ $3^6 = 729$

$$\ln(y) \overset{?}{=} 6\ln(3)$$

$6.592 = 6 \cdot \ln(3)$ $\underline{\underline{\text{yes}}}$.

Since $\ln(y) = 6 \cdot \ln(5)$

$$\hat{f}(MW, VP, DP) = t_r^{C_6}$$

$$\ln\left(f(MW, VP, DP)\right) = C_6 \cdot \ln(t_r)$$

$$C_6 = \frac{\ln\left(f(MW, VP, DP)\right)}{\ln(t_r)}$$

if $y = \boxed{\begin{matrix}\dfrac{\ln(5)}{\ln(3)} \\ 1.46\end{matrix}}$ does $e^y \overset{?}{=} \dfrac{5}{3}$ (1.67) $\underline{\underline{\text{NO}}}$!!

$$\ln\left(\frac{a}{b}\right) = \ln(a) - \ln(b)$$

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Now look @ Ethane @ 80°C @ 1.36 min.

We did something ~~interesting~~
We combined all equation methods
together into a single mean.
We get a clear difference in the value of

		MW	VP	DP
4.12m (meas)	4.15m (calc)	44	-70	.03
1.34m (meas)	1.23m (calc)	28	-150	0

Now look @ values for Propane & Ethane

(actual)	Propane	44	-42	.08
(actual)	Ethane	30	-90	0

You can see that you
have no difficulty whatsoever
distinguishing these two from each other.

		For instance Propane Actual	44	-42	.08
		VS			
Σ	3	Calc ~~meas~~	① 44	① -70	① +.03
Σ	6	calc ~~meas~~	② 28	② -150	② 0
		Ethane Actual	30	-90	0
		VS			
Σ	5	calc ②	44	① -70	② .03
Σ	4	calc ①	28	② -150	① 0

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but we also have

$$f(MW, VP, DP) = e^{C_6 \cdot \ln(tr)}$$

but $e^5 \cdot e^3 = e^{5+3}$ $e^{(5\cdot3)} = 3269017$

$y = e^{b \cdot x}$ $y = e^{b \cdot \ln(x)}$

$\ln(y) = [b \cdot \ln(x)] \cdot \ln(e)$ but $\ln(e)$ is a constant. it equals 1

so

$$\boxed{\begin{array}{l}\ln(y) = b \cdot \ln(x) \\ y = e^{b \cdot \ln(x)}\end{array}}$$

$y = ax^b$

or

~~$\frac{\ln(y)}{b} = \ln(x)$~~ $\ln(y) = b \cdot \ln(ax)$

let $a = 1$ $\ln(y) = b \cdot \ln(x)$ $b = \frac{\ln(y)}{\ln(x)}$

So this is correct.

~~let b=2~~ let b = 1.5   let a = 1

ln(x)	x	y	ln(y)
	1	1	
	2	2.83	
	3	5.20	
	4	8	
	5	11.16	

yes, regression does give us $y = 1.00x^{1.50}$

$y = ax^b$

$y = ax + b$ use linear regression solved using $\ln(x)$, $\ln(y)$

$y = 1.50x + 0.00$

↑ " "

this is b

it is the slope

This works with a single variable regression.
I don't think so with a multivariate regression.

Our problem here is that we were led to a plateau prematurely.

We did not like using the ln(tr) as it ~~seems~~ to taper off too quickly.

But now we see that a linear model does not taper off quickly enough.

So we are proposing a power model but the problem is that we do not know how to solve for it using a multivariate function.

The idea is probably correct.

$f(MW, VP, DP, T, Cw) = tr^b$

But how to solve for B?

trial and error is one way. We know that $b < 1$

We certainly can use $tr^{1/2}$. of $\sigma_s = 1.9$ min

tr Power	σ_s
1/2	.38
1/3	.20
1/4	~~.0~~ .13
.2	.10
.1	.04

But then the Coefficients vanish toward 0.

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Let us adopt

$f(MW, VP, DP^{1/3}, T, C_0) = t_r^{1/3}$ This leads to $\sigma_S = 0.20$

if $f() = \ln(t_r)$ $\sigma_S = 0.40$

error

So it cut it by 1/2

~~MW C_1 5.418E-3~~
~~VP C_2 3.001E-3~~
~~$DP^{1/3}$ C_3 .609~~
~~T C_4 -4.47E-3~~
~~C_0 C_5 1.611~~

Note!

But $f(\quad) = t_r^{1/4}$ $\sigma_S = 0.13$ min

Seems even better 1/3 err

MW $C_1 = 3.216E-3$
VP C_2 2.275E-3
$DP^{1/3}$ C_3 .414
T C_4 -3.066E-3
C_0 C_5 1.457

$\sigma_S = 0.13$ min

σ_S

MW: $t_r^{1/4} = .019\,MW - 2.481E\text{-}3\,T + 0.678$ 0.19

or

$t_r = (.019\,MW - 2.481E\text{-}3\,T + 0.678)^4$ ~~0.16~~

VP: $t_r = (4.001E\text{-}3\,VP - 2.852E\text{-}3\,T + 1.825)^4$ 0.16

DP: $t_r = (0.83\,DP^{1/3} - 2.662E\text{-}3\,T + 1.273)^4$ 0.19

OK, the model is now working.

I see what some of the problem was

For low Cn (ie C_1 - C_4) you need to use the low temperature segment of the model

For C_5+ you must use the mid segment of the model ie 150°C.

you reserve 220° for high Cn candidates in the future and for the investigation of polar molecules.

You are on the right track now with low error coefficients.

OK, you can investigate anything you want.

Use the appropriate temperature range.
Use more than one template if there remains doubt.

Example

N_2 @ 80°C tr = 0.35 min.

We have an approximation of MW=15 VP=-210 DP=0.00

We get the same results for O_2.

	MW	VP	DP
N_2	28	-196	0
O_2	32	-183	0

Nothing else comes close to this other than Co but it has a dipole moment of 0.11.
These gases are pegged.

You can also solve this @ 40°C

We get	MW	VP	DP
N_2	10	-230	0.00
O_2	10	-230	0.00
vs			
	28-32	-183-196	0.00

Not bad. 80°C is sufficient, 40°C is tolerable

Now for CO_2 @ 80°C tr = 1.61 min

	MW	VP	DP
We get	MW = 34	VP = -118	DP = .001
vs	~~32~~	~~-183~~	~~0.00~~
actual	44	-80	0.00

Not Bad!

Now for Ethane @ 80°C tr = 1.36
We get MW= 31.5 VP= -130 DP= 0.0
Actual is 30 -90 0.00
Very Good!

Now for Propane tr = 4.12 @ 80°
We get MW= 49.5 VP= -43 DP= .08
Actual 44 -42 .08

Perfect. This is midrange data.
Now for Propene tr= 5.12
~~us~~ We get MW= 54 VP= -22 DP= 0.15
Actual 44 -48 0.37

Molecular wgt is same, VP is in error and DP is correct.
Not Bad.

We can also do Butane if we would like.
C_1-C_4 OK thru 80°C. tr= 9.57
Might want to do this also @ 150°C and average
Full Evaluation gets a bit high, this is a clue to correct using 150°C.
But we get MW = 67.5 VP= 41 DP= 0.6
Actual is 58 -.8 .13

Now lets look @ ~~180~~ 220°C tr = 2.19 m
We get what appears to be very good results
MW= 57 VP= 5 DP= 0.25
Actual 58 -.8 0.13
Superb

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Therefore we see that butane works very well for 220°C.

This suggests $C_1 - C_3$ @ 80°C & non polar gases
$C_2 - C_4$ @ 150°C
$C_4 +$ @ 220°C.

This also says that if you get dubious results
then apply a different temperature.

We can also try pentane @ 150°C t_r = 3.6 min
Pentane = 4.1 min
Try ~ 4.1 min for average
This yields
MW = 58 VP = 5 DP = 0.300
but I suspect this is too low since
actual MW = 72 ~ 33 ~ .25
Not too bad ~~but MW~~ is too low.
Look @ 220°C 3.28 min?

We get MW = 64 VP = 37.5 DP = 0.5
vs actual 72 33 = 0.3

This yields better results.

This is a great predictive application of the model. We have successfully predicted pentane as existing in the pyrolysis of hair @ 220°C isothermal GC run.
This is your highest gas detected thus far.

I believe hexane is liquid @ room temperature.

Remember the liquid you saw in the pyrolysis of hair!?

There is a very good chance that this is hexane.

You just might be able to distill that off.

BP of hexane is 69°C. C_6H_{14}
IOR is ~1.379

Density is estimated @ 0.7

Pentane has a BP of 36°C

So it is highly volatile.
Hexane is also very volatile but not so much as pentane.

Gasoline has C_4-C_{12} in it, but mostly C_7-C_{11}

C_1-C_4 are gases
C_5-C_7 are solvents

$>C_{12}$ are heavy fuel oils such as diesel

Lets predict how long hexane would take on the column @ 220°C.

MW = C_6H_{14} = 86

Notice this IS the boiling point →

We estimate ~ 10 minutes

We estimate the vapor pressure temp @ ~ 150°C Actual = 68

We estimate the dipole moment @ ~ 2.4 There is NO Dipole Moment.

CRC values are as follows:

MW = 86 given.

Conversion!

1 KPA = 7.5 mm Hg so 100 kPA = 750 mm Hg ≅ 1 atm

So we estimate hexane has a vapor pressure of 1 atm @ ~ 150°C.

An important observation.

The temperature being recorded and used as the VP @ 100 KPA IS essentially the boiling point of the Compound @ 1 atmosphere

SINCE 100 KPA = 750 mm Hg ≅ 760 mm Hg ≅ 1 atmosphere!

So essentially our model IS using the B.P as well as MW as well as dipole Moment.

There appears to be something going on with the bond energies whereby the alkenes elute after the alkanes.

Consider bringing this into your model.

Aug 29 2016

Alkenes vs Alkane elution

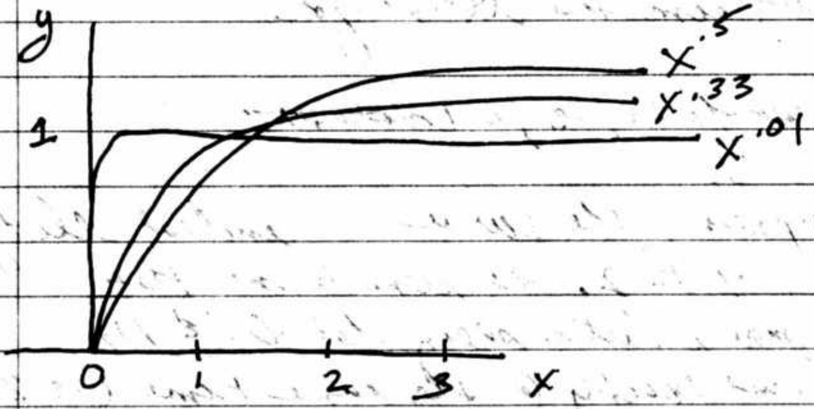
Linear combination of exp harmonic functions

Four Theoretical Prospects:

1. Exp Harmonics
2. Probability Theory
3. GC Physiochemical Modeling
4. Geodetic Anomaly

Now that we have successfully identified pentane on hair @ 220°C
let's add it to the solution
and now also add hexane after pentane has been registered into the model.

Let's look @ the behavior of $X^{1/n}$ series.
Here is what happens



As $n \to 0$, y approaches the constant 1.
This allows for no flexibility in the solution.
It says that all answers drive toward a common value and the error diminishes apparently towards zero but you have no net benefit.

The analysis is actually very satisfactory.

The log functions do seem to have an inherent difficulty. When X (ie tr) < 1, the function should be negative. This does not seem desirable to me. ie, $\log_{10}(1) = 0$ and $\ln(1) = 0$.

since tr is often < 1 it seems to me the f matrix, if you chose the log or ln function should have $\ln(tr+1)$ as the f matrix.

this initializes $tr = 0$ as $\ln(tr) = 0$. Yes this is true. So this should have been the first move.

Second observation is that $\log_{10}(x+1)$ and $x^{1/4}$ are incredibly similar except for

1. an offset factor, ie, a constant
2. The sharpness of the curve @ initial elution periods, ie $x < 2$. It seems to me that $x^{1/4}$ is probably more realistic seeing that O_2 & N_2 come out almost exactly @ the same time (ie 0.35 min) regardless of the temperature.

The analysis is actually quite revealing.

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We also see that there is a difference between the slope of the $\ln(x+1)$ function and the $\log_{10}(x+1)$ functions

absolutely!

but that you can make them ~~almost~~ identical with a scaling function, so either one can work.

$$\log_{10}(x+1) \cong 0.45 \ln(x+1) \qquad \frac{\ln(2)}{\log_{10}(2)} = 2.303$$

so the two functions ~~[illegible]~~ differ only by a ~~constant~~ ratio. and $\frac{1}{2.303} = .434$

$$e^1 = 2.718 \qquad \frac{\ln(3)}{\log_{10}(3)} = 2.3025$$ it is the same

$$10^1 = 10$$

~~Let x~~ $\frac{\ln(4)}{\log_{10}(4)} \overset{?}{=} C \qquad \ln(4) = C \cdot \log_{10}(4)$

^ This is true but how do you know that this is true? $C = 2.3025$

$$\frac{\ln(10)}{\log_{10}(10)} = \frac{\ln(10)}{1} = \underline{\underline{2.3026}}$$ This is how you know.

What we see is that $x^{0.21}$ actually has a slope that is almost identical to either log function for $x \geq 2$.

Basically we take the ratio of the derivatives to find this answer.

$y_1 = \ln(x+1)$ $\qquad y' = ?$

$y_2 = \log_{10}(x+1)$ $\qquad y' = ?$

from CRC:

$$\frac{d(e^v)}{dx} = e^v \frac{dv}{dx} \qquad \frac{d(\log_a v)}{dx} = (\log_a e)\left(\frac{1}{v}\right)\frac{dv}{dx}$$

Therefore if $v = x+1$

$$\frac{dv}{dx} = 1$$

Therefore

$y = \ln(x+1)$ $\qquad y = \log_{10}(x+1)$

$y_1' = e^{x+1}(1) = e^{x+1}$ $\qquad dv/dx = 1$

$$y' = \log_{10}(e) \cdot \frac{1}{x+1}(1)$$

$y = ax^b$

$y' = b \cdot a \cdot x^{b-1}$ $\qquad y' = \dfrac{\log_{10}(e)}{x+1}$

and if $a = 1$

$y_2' = b \cdot x^{b-1}$

Therefore, to construct our ratio of derivatives of the power function to the ln (function) we have

$\frac{y_1'}{y_2'} = \frac{e^{x+1}}{b \cdot x^{b-1}}$ Now let's assume the ratio equals a constant.

C = Constant slope ratio when $x \to \infty$

$C = \frac{e^{x+1}}{b \cdot x^{b-1}}$ or

b = exponent to pow fnx.

However, we wish to assume that C = 1 (!) Therefore

$b \cdot x^{b-1} = e^{x+1}$ as $x \to \infty$

$b = \frac{e^{x+1}}{x^{b-1}}$ let $x = 100$ $b = \frac{e^{101}}{100^{b-1}}$ $b = \frac{e^{3}}{100^{b-1}}$

Something seems wrong here.

let $x = 4$ $e^5 = 148.4$

$b = \frac{148.4}{4^{b-1}}$ or $b \cdot 4^{b-1} = 148.4$ $b \cong 3.67$

$1/3.67 = 0.27$

now let $x = 10$

$b = \frac{59874}{10^{b-1}}$ or $b \cdot 10^{b-1} = 59874$ $b = 5.07$

$1/5.07 = 0.20$

Surprisingly close to our estimate of $x = 0.21$

let $x = 20$: $b \cdot 20^{b-1} = 485,165,195$

$b \cong 7.025$

$1/7.025 = 0.14$

This says that it is hardly a constant slope but that $y = x^{1/5}$ is actually a fairly decent choice. And that it is slightly better than $x^{1/4}$.

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You see now that you have two choice in your model.

1. 1st you should check that pentane is added to the input matrix.

2. When this is done, you should add hexane using the time estimate from the MW, VP + DP data @ 220.

3. When this is done, you can select either

$\ln(X+1)$

or $X^{1/5}$ power

and evaluate the error of both. The error term should be similar.

First step is to see if pentane is added @ 220°C with $t_r = 3.28$ min.

No, it is not added and it needs to be.

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Aug 29 2016

Our latest model now with

1. An additional pentane added
2. A projected hexane added
3. $y = ax^{0.20}$ adopted vs $y = ax^{0.25}$

based upon an analysis of the power function compared to the log function

$\sigma_s = 0.103$ min.

$y = [f(t)]^{1/5}$

C_1 5.083E-3
C_2 1.63E-3
C_3 0.234
C_4 -2.157E-3
C_5 1.234

Error of ln(x+1) Exploratory Model is 0.40 (σ_s)
This says our power rule seems to be much better

MW: $t_r = (.014\,MW - 1.963E\text{-}3\,T + .779)^5$ $\sigma_s = 0.14$

VP: $t_r = (3.152E\text{-}3\,VP - 2.091E\text{-}3\,T + 1.628)^5$ $\sigma_s = 0.12$

DP: $t_r = (0.536\,DP^{1/3} - 1.217E\text{-}3 + 1.167)^5$ $\sigma_s = 0.18$

We have an estimate for hexane now incorporated into the model. Nothing is perfect but it provides a reasonable first estimate as to what to expect. The lack of polarity in hexane is somewhat analogous to the model.

$\tilde{t}_r$ = ~8 min @ 920°C

We have done well w/ the model and have accomplished what we were after.

1. The model has been adapted with a $y=ax^b$ of $y=ax^{1/5}$ due to parallelism w/ the log function but w/a steeper rise from 0-2 min.

2. The error of the power law regression is considerably lower than that of the ln(tr+1) function $\sigma_s = 0.10$ min vs $\sigma_s = 0.40$ min. This difference is significant.

3. We have now verified pentane @ 150°C and we have projected hexane. We can now push GC further, including higher hydrocarbons, Esters and Ethers. We can also start pulling mild but increasing polarity into the column.
   MEK might be a good one after distillation or Acetone?

4. One thing that is very interesting is to predict the character of the contaminants in the rainwater.

With water from ramyad we have some ~~enteresting~~ behavior

$t_r = 4.276$ @ 220°C
MWt = 18 Considering all average
VP ≅ 100 ✓ we get 3.73m $\bar{X} = 4.19$ min
DP ≅ 1.85 & 4.65m amazingly close to meas. 4.28!

for the water Contaminant @ 64.36 min we estimate
MW = 140 gms/mole $n(12) + 2n \cong 140$
(actually B.P.) @ 1 atm VP = 360°C $n(12+2) \cong 140$
DP ~ 18 (extremely high is 8-9) $n = 10$
estimate DP @ ~3.0 $\Rightarrow C_{10}$

3 Regression mean 65 min
Full evaluation 136 min. Major divergence here.

~~100 kPA~~ BP ≅ 360°C
750mm

You could now start experimenting again w/ adding water to the model.

Aug 30 2016
Back to Wallace and to the lab.
This could be your last main run in the lab before heading south for the winter.

You really need to think about what you want to work on.

[redacted]

[redacted]

This year you have learned a lot about
1. Rainwater
2. Distillation
3. GC

These seem to be the three main projects worked on. GC has been your focus and you are indeed far more comfortable with it.
4. Fundamental properties is also a benefit.
5. IR search capability - database.

6. Community Health Professional Network has been created.

7. You have made a GC model that is quite fascinating.

Another question that is arising is whether I can create a multivariable regression using exp. harmonic basis functions.

Can we set up

$$C_0 + C_1 e^{-x} + C_2 x + C_3 e^{-y} + C_4 y = l_1$$

is this any different from?

$$C_1 MW + C_2 VP + C_3 DP^{1/3} + C_4 = l_1$$

MW, VP, $DP^{1/3}$ etc do not need to be linear,
only the form needs to be known.
Therefore we see that we can do this.

Assume a 4 order term + p(x)

eg for MW $y_1 = {}_1C_0 + {}_1C_1 e^{-x_1} + {}_1C_2 \sin(x_1) + {}_1C_3 \cos(x_1)$

eg for VP $y_2 = aT + b$

Do the x's have to be the same point in both cases? actually they do not.

So the model that develops is

$$C_0 + C_1 e^{-MW} + C_2 \sin(MW) + C_3 \cos(MW) + aT = f_1$$

with all MW terms must be between 0 & 2π

This most certainly seems feasible

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What you have not done

1. The Environmental filament work has not been comprehensive, you made one major run.

2. The DNA work has not been done w/ electrophoresis

3. The protein work has not been done w/ Edvotek labs.

4. Culture sheets have not been completed.

You seem to be especially interested in GC and learning what its capability is. You love to separate and to identify unknowns.

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With GC you would like to introduce a slightly higher Carbon no (eg hexane) and a slightly polar substance.

[redacted]

Acetonitrile
Aniline
Cyclo hexanol
Benzaldehyde
Benzene Crystallizable
Benzyl Alcohol
Carbon Disulphide
Dimethyl sulfoxide
Ethylene Chloride
Ethylene glycol monoethyl ether
Nitrobenzene
Propylene glycol
2 Propanol
Methanol
Octanol
Xylene

We start the session by distilling methyl ethyl ketone from True Value.

1st fraction.

64°C – 68°C

It dissolves plastic tubing

Seems to stabilize the most @ 68°C.

We dissolved the plastic tubing
After stopping the operation, the impurities left from the rubber stopper settled back into the beaker.

Our initial onset was at 58°C. I believe this was pure acetone. Now it is slowly climbing again to 67°C. This seems to be our pure material.
Also we replaced the plastic tube w/ 70" of length w/ ~~[illegible]~~ ~~brass tu~~ brass tubing. This is working much better.
68°C is definitely a reference point.

Letting it cool down after initial heating does settle the impurities back into the beaker.

Now we are @ 70°C
~~Then we have 71°C~~

Ok, we are going ahead with the second iteration of distillation of MEK. We seem to have 2 different fractions. One @ 68°C & the other @ 70°C. There also appear to be some acetone that came out up front.

This material is highly flammable & volatile so be cautious.

SET 1

F1 = 50°C (could be boil over)

F_2 = 63°C - 65°C

F_3 67°C

F_4 69°C

F_5 70°C

It is dissolving the plastic tubing. Not good.
You are getting a lot of impurities.

I have removed the plastic tubing.

Now for the 70° batch.

50° again (overflow)

63°C - 65

67

70

The lower temperature material is what is dissolving the plastic & rubber. I believe it to be acetone.

Lets go get the 54°C series.

First elute is actually 61°C - 62°C
It was because of too much material
It's acetone

There is no 50° material. It was overflow.

	Brix	IOR
64	28.2	1.376
67	27.9	1.375
70	27.6	1.375

It is declining.

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Now pure acetone (True Value) reads 18.4

so we know that our 64° elute is not pure acetone

Candidates from Colly are

64D 10R 1.376
  2 Methyl Propanol
  Hexane
  2 methyl Pentane
  3 methyl Pentane
  Methyl Sec Butyl Ether

67D 10R 1.375
  2 Methyl Propanol
  Hexane
  3 Methyl Pentane
  Methyl Butyl Ether

70D Butanal
  Dimethyl Propanol
  Hexane
  Methyl Butyl Ether
  Ethyl Tert Butyl Ether

MEK says
Butanone on
MSDS

Butanone is
known as MEK

Aug 31 2016

Continuing w/ distillation & separation of MEK.

1st step is to Calibrate the thermometer w/ water.
You can't really tell what you have got.

There is also some contamination on the heater.
As well as the fractional Column.

With purported water we have a first fraction
@ 89°C. - 90°C

It is water coming out. So we do have a
thermometer calibration issue
It could be that every set up is unique
however our 150 ml distillation flask
is clearly showing itself to be 8°C low.
This explains our difficulties last night.

Our 70°C BP was actually 78°C.
And the BP of MEK is 79.6°C
and with a 2° elevation differential we
cannot get any better than that.

We also matched w/ the IOR so we pegged
butanone (MEK) to a tee w/ both the BP
and the IOR.

Now it is also possible that our rubber stopper contamination did indeed create a new product.

The BP of that solution should be 64° + 8 = 72°
When we add the 2° elevation differential
we get a compound w/ a BP of 74°C
and an IOR of the same as MEK.

Guess what? Butyraldehyde has a BP of 75°C
and an IOR of 1.377
We got 1.3766

So then is what has happened.

1. We do have a thermometer calibration difference (it really should not be considered an error, it is indeed a calibration.

2. The rubber stopper contamination (we see that MEK eats plastic!) created the formation of a new compound and the GC w/ detecting them also. There is our very broad peak that is showing up after about 50 minutes into the cycle.

3. We have eliminated most of the plastic contamination w/ the use of brass tubing and an aluminum foil junction.

Our contamination looks like it is working itself out of the fractional column.

Saran wrap makes even a better connection than foil and allows for better resolution.

The other flask probably needs to be calibrated as well.

Check our contamination of the water w/ IOR.

The Brix of the mildly contaminated water is 0.3

This is inconsequential.

Questions:

1. Can we use headspace w/ MEK?
2. Can we use headspace w/ Gasoline?
3. Can we use pyrolysis w/ an evacuated chamber?
4. Can we evaluate the HEPA filter residue?
5. Can we increase the ~~CO_2~~ CO content of CDB culture?

Ok we are now calibrating the 500ml flask. Things are all very good.

Density of 70° MEK sample

$$\frac{7.91\text{ gms}}{10\text{ ml}} = \frac{.791\text{ gm}}{\text{ml}}$$

Theoretical density is .805

So		meas	theoretical
1	Boiling Point	80°C	79.6°
2	Index of Refraction	1.375	1.379
3	Density	0.79 gms/ml	0.80 gms/ml

You certainly cannot do any better than that! You pegged it!

Now we are distilling water in the 500ml boiling flask for calibration purposes.

Some contaminants are coming out first @ 86°C.

We learn that the fractional column for the 500 ml flask is behaving exactly the same way. Mean difference w/nt elevation 4.5 - 8°C. Things are great.

Aug 31 2016

We are studying a crystal form received from CA in Jun of 2013.

We have completed some important solubility tests.

It is water soluble.
It also dissolves in both KOH & 5% baking soda solution, so then indicate that it is acidic to some extent.

It is **NOT** soluble in Ethylene Glycol Monoethyl Ether

Ether solubility is an important defining characteristic.

Let's see what the IOR of a solution is.
Brix is 2.4
This leads to IOR of 1.335 vs 1.332 for water.

~~Two~~ One items have a IOR of 1.335 in Colby

Acetaldehyde

C_2H_4O but BP is 21°C! and MP is -125°C

MP of our crystal is $\geq 180^\circ C$

Sep 01 2016

On we go!

The pH of the Carpenteria crystal is 8.1 in H_2O
Not what I suspected since it reacts w/
1M NaOH & 5% sodium bicarbonate.

Our first assessment is that it's an ionic crystal. I presumed an acid salt but now I have my doubts again. It seems as though it could be basic. Maybe it has both.

Today I want to:

1. Continue w/ the CO project on the COB Cultures
2. Continue w/ the crystal
3. Always continue w/ GC.
4. Conductivity of Crystal!

5. Always regrouping on the general projects
    1. Env Filament
    2. Electrophoresis - DNA
    4. Protein Labs
    5. Hepa Filter Analyses
    6. Gasoline on GC?
    7. Protein Analyses
    8. Culture Seals

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OK, the crystal is important.

Properties thus far.

1. Index of refraction of dilute solution is 1.335

2. It is water soluble
3. It is not soluble in ether
4. It reacts and dissolves in NaOH
5. It does not dissolve in HCl
6. pH of dilute solution measures @ 8.1 8600
7. Conductivity is extremely high ~ ~~7500~~ PPM ~~8500~~
in dilute solution of distilled water
~ 1mg in ~ 20ml of H_2O
This is extremely high.

8. Presumed to be ionic @ this time
9. Melting point is > 180°C - torch already
10. Table salt measures ~ 2000 PPM
This is a highly conductive material

You need to know what elements it contains
Electrochemistry is your path.

No indication of positive metal ion
But we must also use ammonia

CDB shows no production of CO from culture @ room temperature. Half of cultures are now elevated to ~ 90°~~C~~ F.

CO_2 production is relatively high ~ 1.25% of total

1% = 10,000 PPM.

The balloons also did not show any visible gas production as they have before.

A propane torch goes up to 2000°C

Map gas goes up to ~ 3100°C.

No wonder you fried your thermometer.

We do have a peak @ 10.1 min.

I have done well today.

1. Crystal conductivity discovered.
   Electrochemical study is next.

2. Crystal has been melted @ ≤2000°C.
   Need new thermometer.

3. GC analysis of CDB culture continues.
   All goes well there.

4. IR analysis of HEPA filter has started.
   It has strong similarity to the protein complex.

Now for a little nap. Electrochemistry of crystal soon..

Normal Pulse Differential Analysis of Carpleventrea N Crystal.

We have peaks identified at

-2.92V K = -2.92 Sr = -2.89
Ba = -2.9
-2.56V La = -2.52
Ac = -2.60
-2.27V Yb = -2.27 H_2 = -2.25
$Al(OH_3)$ = -2.31
+ 0.76V Fe +.77
Zn -.76
1.00V HO, H^+, H_2O +.99

Notice how much less the sample is complicated than the rainwater sample is.

Let's look @ the crystal form

Flame Test - Lavender
Solubility - In water
Not in ether
Electrochemical - Redox @ -2.92V
Glycerol solubility?
Melting Point > 250 [770°C] < 2000°
Appearance - white crystalline solid.
Face centered cubic structure
Have prepared conductivity solution

The sheet is wrong

$$\frac{0.14 \text{ gms}}{200 \text{ ml}} = \frac{0.70 \text{ gms}}{1000 \text{ ml}} = 9.39E-3M$$

???

$$\frac{9.39E-3M}{.01M} (111.8 \text{ mS/cm}) = 104.98 \text{ mS}.$$

We measure 1350uS = 1.350mS???

Assume 2.5% KCl = 500 uS/cm^{-1}

$$2.5\% = \frac{2.5\text{gms}}{100.\text{gms } H_2O} = \frac{x}{200\text{gms } H_2O} \quad x = 5\text{gms}$$

We have ~ 0.01M Solution (200ml, .14gms)
w/ $\sigma \cong$ 1350 uS

A calibrated solution of pure KCl has
a conductivity of ~ 2500 uS.

So our solution is not pure and it does
have other elements in it.

Either way it is still highly conductive.

Compare conductivity to NaCl?

Also Potassium Chloride Brix came out to be 0.0
Not 2.4 like our crystal. So something is
different.

Sept 03 2016

Today we want to:

1. Run the GC CDB tests.

2. Pursue the lanthanum question more seriously now.

3. The CDB residual is showing what appears to be a broad peak? Room temperature incubation. You can see that the cultures behave differently under heat and the solution does clear up.

Crystal Comparison

Potassium Chloride

Meas	Theoretical
Redox -2.92V	-2.92V
Flame Test: Lavender	Lavender
High Conductivity .01M Solution 1350uS (0.14gms/200ml)	Control KCl Solution meas. as 2500uS
Soluble in Water Not Soluble in Ether Soluble in glycerol Slightly soluble in alcohol	Soluble in Water Not Soluble in Ether Partly soluble in glycerol ??
Melting Point >250 <2000	770°C
White Crystalline Solid ? ? ?	White Crystalline Solid Cubic like NaCl
Index of refraction 1.335	1.332 by Control

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Lanthanum Chloride

Mea

Theoretical

Soluble in water, ethanol

MP 858°C

White odorless hygroscopic
powder
Hexagonal Crystal

What phosphate do we have?
We have lots!
Sodium Phosphate
Phosphoric Acid

Mixing the crystal w/ KOH/NaOH solution is creating a great deal of heat.

KCl mixed w/ NaOH + KOH does not generate heat.

Mixing the crystal + Conc. HCl does not show any reaction

OK, none of these has relevance to the crystal.

Conc KOH, NaOH + Conc HCl create a lot of heat
WITHOUT THE CRYSTAL!
The crystal has nothing to do w/ the heat.

Lanthanum needs Ca ion in addition to phosphate?

There is indeed some cloudiness to the water taking place when you combine
1. Sodium Phosphate
2- Calcium Hydroxide
3. The Crystal
4. Water.

This does suggest the possibility that phosphates are likely removed from the solution.

We may indeed have something here.
We need to repeat under tight controls
& clean test tubes.

Good news on the COB - CO Testing.

We have CO detectable again after several runs w/ no detection.
Conditions are:
1. Room incubated for 18 hrs. Not detected
2. Placed in incubator @ ~95° for 25 hrs
3. First run shows no detection
4. Second run clearly shows CO detection

Only thing done differently between 1st & 2nd run is that I cleaned the syringe thoroughly w/ acetone including thorough evaporation. Is it possible that a dirty needle was interfering w/ CO, ie from the hair pyrolysis & tar that resulted?

Not only that, we are getting a second definite peak @ about 12.5 min. I believe we have seen that before.

Crystal test for [illegible]
Controls include

1. Crystal in Water Only

2. Sodium phosphate & Calcium hydroxide only

3. Crystal in sod. phosphate + Ca Hydroxide

GC we are getting a lot of activity w/ the CDB culture now. We must use the high current.

We also have another spike!
The CDB gas does have some odor to it,

Notice that there is some kind of peak prior to N_2/O_2

You forced the balloon air gas back into the tube before extraction.

Low current may end up being more sensitive than high current?
Moderate incubation of 94° may have lower improved gas production.

There is indeed a distinctive odor to the CDB gas production.

There does appear to be some crystal interaction - chemistry & formation occuring between the

Carpenteria Crystal
and
Calcium Hydroxide - Sodium Phosphate
Combination.

Photographs have been taken of

Carpenteria alone	cubic & rectangle
Ca & PO4 alone	asymmetric diamond
Carpenteria Crystal + Ca + PO4	diamond Symmetrical

Idea on melting point determination

$$Q = mC\Delta T \qquad Q_2 = Q_2 \Rightarrow \overset{\text{boat}}{\underset{\uparrow\ \text{measure}}{M_1}\,\underset{\uparrow\ \text{find}}{\dot{C}_1}\,\underset{\uparrow\ \cancel{\text{measure}}\ \text{Calc}}{\Delta T_1}} = \overset{\text{water}}{\underset{\uparrow\ \text{meas.}}{M_2}\,\underset{\uparrow\ \text{find}}{C_2}\,\underset{\uparrow\ \text{meas}}{\Delta T_2}}$$

$$\Delta T_1 = \frac{M_2 C_2 \Delta T_2}{M_1 C_1}$$

$$q = \overset{\text{specific heat}}{S_p}\, m\, \Delta T$$

We are going to work on a melting point temperature.

First, determine specific heat of the metal container, and its mass

Mass of water = 150 gms.
Mass of container = 9.98 gms

Temperature of water (start) = 22.9
Temperature of container to start = 120°c
Specific heat of water = 4.184 kJ/mole (?)

Temperature of water to end 24.5°C

$q_1 = m_1 C_1 \Delta T_1$ $q_1 = q_2 \Rightarrow m_1 C_1 \Delta T_1 = m_2 C_2 \Delta T_2$
$q_2 = m_2 C_2 \Delta T_2$

solve for C_2

1 = metal container
2 = water.

$$C_2 = \frac{m_1 C_1 \Delta T_1}{m_2 \Delta T_2}$$

$$q_2 = m_2 C_2 \Delta T_2 = (150\,\text{gms})\left(\overset{\text{Joules/gram C°}}{\cancel{4.184}}\ 4.186\right)(24.5 - 22.9) = \cancel{1004.2}\ \text{Joules} \quad 1004.6\,\text{J}$$

$$= \frac{\text{gms} \cdot \text{Joules}}{\text{grams} \cdot \text{C°}}\ °\text{C} = \text{Joules}$$

$$q_1 = m_1 C_1 \Delta T \Rightarrow C_1 = \frac{q}{m_1 \Delta T} = \frac{\overset{1004.6}{\cancel{1004}}\ \text{Joules}}{9.98\,\text{gms}\ (120 - 24.5)}$$

Specific heat of container $= 1.053 \frac{\text{Joules}}{\text{gm C°}}$ 1.06

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A net table shows the specific heat of stainless steel being ~ 0.50 J/gm°C.

How can we differ by this much?

Lets do it again.

With net example, he does get a value of 1.20 J/gm C
This is pretty close to me.

We were correct: $C_2 = \frac{m_1 C_1 \Delta T_1}{m_2 \Delta T_2}$ $\quad \frac{\cancel{79}\ 150 \cdot 4.186 \cdot (24.5-22.9)}{9.93\,(120-24.5)}$

But almost all metals $\quad = 1.06\ J/gm \cdot C°$
have a much lower value
for specific heat, eg < 0.5
So why do we end up with this?

T_0 Calorimeter = 23.2 $\qquad$ T of water = 96.5°C
T_F 23.7°

m of vial 9.99 gms $\qquad C_2 = \frac{150\,gm\,(\overset{J/gm\,C}{4.184})(23.7-23.2)}{9.98\,gm\,(96.5-23.7)}$
m of H_2O = 150gms

OK, much better. $\qquad = 0.432$

Therefore your temperature of the metal must have been off.
Yes the metal was hotter than you thought.

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Your temperature of the vial was higher than you thought. It must have been about 170-180°
Actual it had to be about 220°

Actually, the thermometer placed in the sand gave the best result 227°C

$\Rightarrow C_1 = 0.50$ which is exactly correct for stainless steel.

So the real answer was $C_2 = \frac{150\,\text{gms}\,\overset{\text{J/gms/°C}}{(4.184)}(24.5-22.9)}{9.98\,\text{gm}(227°-24.5)}$

$= 0.50$ J/gm·C which is perfect for stainless steel as looked up in a table.

Now we have a good specific heat and we can melt the crystal.

Our equation is $\Delta T_2 = \frac{m_1 C_1 \Delta T_1}{m_2 C_2} = \frac{150(4.184)(27.1-22.9)}{9.90(0.50)}$

ΔT ~~MP~~ $\cong$ 528°C Good Job

→ above room temperature.

So add 22.9 = 551°C
MP

It worked!

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Caloremetry Methods.

Instruments needed

1. Probe 9 Detailed Thermometer
2. Scales
3. Calorimeter
4. Heat Source
5. Table of specific heats.

Relatively simple equipment needed. Very clever

~~Sepo:~~

$$\Delta T_2 = \frac{850\text{gms} \overset{\text{(water)}}{} \overset{\text{J/gmC}}{(4.184)}(37.8-20.3)}{138\text{gms}(\cancel{.49})\,\boxed{.72}} \quad \text{Revise}$$

$= \underline{\underline{920.4°}}$ Amazing.

$$\begin{aligned} \text{So it is } &\geq 920.4° \\ &+ 20.3 \\ \text{MP} &\geq 940.7 \end{aligned}$$

We estimate the MP is > $\underline{\underline{950°\text{C}}}$ Potassium Sulfate

~~Volume of~~ Mass of graduated Cylinder = 20.09 gms
Volume of Material = 6 ml (= 6 cc)
Mass of Material = 7.51 gms

$\text{Density} = \frac{7.51\text{gms}}{6\text{ cc}} = \frac{1.25\text{gms}}{\text{cc}}$ Potassium Sulfate is 2.66 not a match

Sep 03 [redacted]

Continuing w/ M.P. ~~determinat~~ ion and specific heat.
I have a pipe cap now. This will be better.

Water @ start = ~~20.5~~ ~~20.9~~ ~~21.1~~ 21.2
Water @ end =

Specific heat of Carbon steel = 0.49

Pan method:

Water mass ~~1167 gms~~ 850 gms

Initial Water Temp ~~20.7°~~ ~~20.1°C~~.
~~20.4~~ 20.3°C

T final = ~~37.7°C~~ 37.8°C
Now calculate

Need mass of plg: 1389 ms

Cp Carbon Steel = 0.49

ΔT_2

Primary physical properties

1. Ionic
2. Conductive
3. MP > 950°
4. Density ≈ 1.25 gms/cc (actually a little more Estimate 1.36 maybe 1.5 gms)
3. Flow Test Lavender
4. Electrochemical K & Ca
5. Soluble in H_2O
6. Insoluble in Ether.
7. Partly soluble in glycerol?

Sep 03 2016

1. We want to use the melting point of NaCl as a reference point and control

2. We want to use the cultures in GC

3. We want to continue to identify the crystal.

NaCl Melting Point Analysis

T water initial = ~~19.5°~~ 19.6°

Mass of H_2O 850 gms
It went to ~~41.5°C~~ 41.4

$$\Delta T_2 = \frac{850\text{gms}(4.184)(41.4-19.6)}{138\text{gms}(.49)}$$

= 1146°.5 C and this is too high. + 19.6 = 1166
It is actually 801°C
It was showing 1st signs of melting.
I wonder if specific heat should be chosen @ .70
$\frac{801}{1166}$ = ~~.49~~ vs 0.49?
~~.50~~ .72

$$\frac{850(4.184)(41.4-19.6)}{138(\cancel{.49}\ \cancel{.50}\ .72)} = \cancel{814°C} = \underline{800°C}$$

So we are going to use 0.72 for Cp of the crystal right now.

Now reapply this to K which did not melt:

$$\Delta T_2 = \frac{850\,gm(4.184)(37.8-20.3)}{138(.72)}$$

$$= 626^\circ + 20.3 = \cancel{646}\,647^\circ \approx \underline{\underline{650}}\ \}$$

Actual valu is $\underline{\underline{770}}$°C.

OK, now lets head toward something more approachable,

Ammonium sulfate 235°C
Sodium Hydroxide ~~604°C~~ 318°C

Now the pipe weighs $\underline{137}$ gms,

Ammonium Sulfate Trial

pipe = 137 gms
H_2O initial = 850 gms
H_2O initial temp 21.0°C
T final 28.8°C

$MP = T_0 + \Delta T$

$$\Delta T_2 = \frac{850(4.184)(28.8-21.0)}{137(.72)} = 281.2$$

actual is 235. not too bad.

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Think about this. $Q_{\cancel{F}_2} = m_2 C_2 \Delta T_2$

$Q_w = M_w C_w (T_{F_w} - T_0)$ $Q_p = M_p \cdot C_p \cdot (T_{F_p} - T_0)$

~~$MP = T_{F_2}$~~ and $Q_w = Q_p$ P = Pipe F = Final W = water

so $M_w C_w (T_{F_w} - T_0) = M_p \cdot C_p \cdot (T_{F_p} - T_0)$

$M_w C_w (T_{F_w} - T_0) = M_p C_p T_{F_p} - M_p C_p T_0$

$T_{F_p} = \dfrac{M_w C_w (T_{F_w} - T_0) + M_p C_p T_0}{M_p C_p \cancel{T_{F_p}}}$ and $T_{F_p} = M.P.$

This is different than what you had before.

$T_{F_p} = \dfrac{(850\,gms)(4.184)(28.5 - 21.0) + 137\,gms(.49)(21.0)}{137\,gms(.49)}$

This says $C_p \simeq .85$ (This is high.)

Lets go back:

NaCl: $T_{F_p} = \dfrac{850(4.184)(41.4 - 19.6) + 137(.85)(19.6)}{137(.85)}$

$= 646$

Now we are in @ P.B w/ 1st sign of melting. Actual = 801 °C

Crystal Candidate: $T_{F_p} = \dfrac{850(4.184)(37.8 - 20.3) + 138(.80)(20.3)}{138(.80)}$

$= 584$ and we only say > 584

Actual of Potassium Chloride is 770 °C

So this is not out of bounds.

~~Now lets try NaOH~~
Ammonium Sulfate again

$$T_{Fp} = \frac{850(4.184)(28.8-21.0) + 137(.8)(21.0)}{137(.8)}$$

$= 274^{\circ}C$ Actual is 235
This may not be too bad because you allowed it to overheat.

Ab. ~~Now for NaOH~~ (~~313~~°C) Ammonium Sulfate Again

T_{W0} = ~~20.4°~~ 20.5
~~F_W =~~
m_w = 850 gms
m_p = 137 gms
T_F 27.8

$$T_{pf} = \frac{850(4.184)(27.8-20.5) + 137(.80)(20.5)}{137(.8)}$$

$= 257^{\circ}C$ Actual is $235^{\circ}C$.

NaOH reacts w/ lead pipes. Do not use this.

Better. You can hold where you are and adjust
Cmp

It looks like we need to use 0.85

$$T_{P_F} = \frac{\overset{mw}{850}(\overset{Cw}{4.184})(\overset{Twf}{27.0}-\overset{To}{20.5}) + \overset{mp}{137}(\overset{CP}{.85})\overset{To}{20.5}}{\underset{mp}{137}(.85)}$$

= 243°C Actual is 235°C

You can find slurry long stage of visible melting.

—

Lets find something about 500°C.

Strontium Nitrate is 570°C. Perfect

$T_{W_0} = 21.1$

$T_{WF} = 37.2$

$$T_{P_F} = \frac{850(4.184)(37.2-21.1) + 137(21.1)(.85)}{137(.85)}$$

= 512 Actual is 570.
So a little low this time.

Switch to $C_p = 0.84$ Leads to MP = 579
Very good.

Melting Point of a Solid
Using Calorimetry

From all of this, we have a way now to estimate the melting point of a solid, even @ relatively high temperatures.

This is good work and it is a classic application of Calorimetry.

Now we can't try our crystal again.

Your point of measurement is when melting is clearly in progress but not highly advanced. Not just @ the very first edge and not after it is all liquid. There is a mix of liquid & remaining crystal.

The method required calibration of a specific heat using known substance. It differs considerably from the stated theoretical value for steel but it is what is working reliably (i.e. 0.49 vs 0.84 actually used). This might depend upon the actual Calorimeter type that is being used. We might be losing some heat, But this value is working reasonably well.

Now back to the Carp. Crystal

$T_{W_0} = 20.0^\circ$

$T_{W_F} = \cancel{38.5}\ 38.8$

$$T_{P_f} = \frac{850(4.184)(38.8-20.0) + 137(.84)(200)}{137(.84)} \geqq 601^\circ$$

Actually the CC is passing a test for sulfates! Not strong but it is passing.

So we know that the MP is > 600°C. This is the limit of detection. We also know that sulfates are involved.

Looking back, the density could easily be off by a factor of 2.

Let's look @ density of NaCl for example.

Density of salt

$\frac{12.30\text{ gms}}{9.2\text{ cc}} = 1.34$ gms/cc actual is

Actual Density is 2.16 gm/cm3 and this salt is much more finely powdered than our crystal.

I will estimate that it will pack by an additional 25%.

Our current ratio for error is $\frac{2.16}{1.34} = 1.61$

I estimate an additional 20-25% packing
Chose 22.5%
1.225 (1.61) = 1.97 Error Factor estimated

Now recall our computed density of the CC:
We got $\frac{1.25 \text{ gms}}{\text{cc}}$

So with error factor our revised estimate for the density is $1.97(1.25) = 2.44 \frac{\text{gms}}{\text{cm}^3}$

Actual density of potassium sulfate is: $\underline{2.66}$

That is amazingly close.

I would say we are zeroing in

Solubility estimates ~~[illegible]~~ 111 gms / liter
= .111 gms / ml

;; lets add 2 ml to test tube and 0.22 gms
26°C

$\frac{.23}{2\text{ ml}}$ ✓ + $\frac{.12}{2\text{ ml}}$ (.09 dissolves) so $\frac{0.32}{2\text{ ml}} = \frac{0.16 \text{ gms}}{\text{ml}}$

We are now comparing Potassium Sulfate

CC:

Meas	Theoretical (Actual)
Redox -2.92	-2.92
Flame Test: Lavender	Lavender
High Conductivity .01 M Solution 1350 µS (0.14 gms/200 ml)	To be determined.
Soluble in Water. Not soluble in ether Partially soluble in glycerol Alcohol Solubility? Insoluble! Not soluble in acetone	Soluble in water Insoluble in acetone Slightly soluble in glycerol Insoluble in alcohol
Melting Point > 600°C	~1000°C
White crystalline solid	White Crystalline Solid
Passes test for weak sulfate presence	Sulfates present in H_2O
Index of refraction 1.335	To be determined
Density estimate 2.44 gms/cc error = ± 0.5 gms	2.66 gm/cc
Estimated Solubility in Water $\frac{0.16\text{ gms}}{\text{ml}}$ @ 26°C	0.13 gms/ml @ 26°C
Crystal - Cubic? We have images	Crystal - Cubic? We have an image

We will be looking @

Lanthanum sulfate
Chloride
Oxide

Lanthanum
on order

	Sulfate	Chloride	Oxide
	White Solid		
MP	1150°	858°	
H_2O	Slightly soluble in H_2O Soluble in alcohol	Very Soluble Hygroscopic	Insoluble
Density	2.82gm/cm3	3.84gm/cm3	
Crystal		Hexagonal	
Alcohol	Soluble in alcohol	soluble in ethanol & alcohols	
	Difficult to decompose by heat Binds w/ phosphates	Precipitates phosphates (w/ Ca) this lab may have failed. ? But we know we have crystal interaction	

We may have magnesium also if you look @ how crystals formed.

Sep 04 2016

Regroup as always. Let's see where we are at.

1. You have a lot of data on an unknown substance (crystal). The results remain inconclusive.

We have strong suggestions of K & Ca, but they are not proven in their entirety but there is definitely evidence to support their existence.

It might be a lot simpler and more straightforward to run control tests w/ electrochemistry.

You certainly have KCl available.
Also, what is the qualitative tests for Cl^- ions?

You can just test KCl w/ electrochemistry!
That is the purpose & value of the instrument.

2. You have learned a good deal about determining the melting point of a high heat compound. Your method is quite ingenious. You would however, like a much better calorimeter.

3. You have done very well in digging into physical properties, including

1. flame test
2. density
3. index of refraction
4. boiling point
5. melting point
6. specific heat
7. solubility
8. some work w/ GC
9. Conductivity
10. pH
11. ORP
12. Appearance, microscopic crystal analysis

But even w/ all of these, you still have uncertainty w/ respect to an unknown component.
Decrystallization is your next technique to look into.

Electrochemistry really is where it is at.
It is repeatable and controllable, within limitations.
I actually really do like it.

Actually what you see is that electrochemistry now requires a great deal of control work
Also fuel cells, yeast, ØDB etc

Normal Pulse Differential Voltammetry
NP Cards are
Case I (UP) C+3 [-3.2, 3.2]
Case II (UP) C-3 [-3.2, 3.2]
Case III (DN) C-3 [3.2, -3.2]

You forgot to stabilize the reference distilled water curve w/ repetition.
This was not good.

Every time you save the file it creates a new header.

OK, it looks like we have some serious questions on a control run of a KCl.
We have peaks @:

-2.47	Pr?	
-2.08	Sc?	Cl is -2.10 OK
-1.92	FeO_4?, Fe^{3+}, Th?, Am?	N_2+2H_2O is -1.87
-1.42	ZrO_2?	
+0.81	$ClO + H_2O$	is +0.81 OK

But nothing @ -2.92 or +2.92.
What does this mean?

So we are picking up Cl easily but no potassium.

Did we not read once that showing I is very difficult to detect?

Maybe we have some contaminants.
Let's increase concentration and repeat.

I believe we are seeing a case of the difficulty of detecting low levels of K.

I have increased the solution and it appears to be overloaded to me.

—

This is very intriguing. KCl plot is not at all like the Carpenterian Crystal.

And Potassium seems to have a very hard time w/ KCl but not w/ the crystal? CC, that is.

When PC Trace says overload, it stops the current flow so the measurement also stops.

You have an overload in 1 direction but not the other.

There are many lessons here.

Potassium cannot be detected in low concentration.
you had to overload the system w/ a higher concentration (too high) and it scarcely picks it up w/ considerably more error @ -2.85 instead of -2.92.

· This means that there is considerable error and uncertainty in certain cases. Apparently not the Carpenterra crystal but w/ KCl there certainly is difficulty.

So if you are seeing something there you may have to overload but this causes its own problems

There is therefore a balance between the detection of difficult elements and subjecting the system to an overload.

Overloads are not good practice but they can give you limited window important data in certain conditions.

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Overload here did allow the detection of K with error but it would have been lost otherwise.

With the error we have, it is difficult to separate out between
Ca, Sr, Ba, & K
-2.87 -2.88 -2.90 -2.92

Further tests would be required.

We notice though, that we have detected the chloride.
This means we have

$CaCl_2$
$SrCl_2$
$BaCl_2$
or KCl

so you would go to work eliminating the others.

or, there is a way out of this predicament

With KCl @ high concentration, we have peaks @

HIGH Concentration	Low Concentration
-2.89 (lots of error)	
-2.70	
-2.57	
-2.44	
+.72	
+.79	+.81

These are not good. It is inconsistent.

Now lets go for a more modest concentration.

But we still have overload!

We reduce concentration to about 1/4 of what we thought was OK.
KCl is highly conductive!

The work is repeats very well but it is not picking up Potassium ~~at~~ lower concentration.

If the work is very important this shows the value of repeating the tests.

Do not allow major overloads unless you know that you are looking for something.

Someone said you can't pick any Group 1 or Group 2
I think but this is not exactly true.

We got
(1) -2.66 meas and -2.58 Reference
So this value should be disregarded.

(2) We do not get -2.47 this time. It had no meaning to us originally. Repeat tests may be very important.

Our 1st peak of concern @ an appropriate
Concentration is -1.96
This looks to compare to -2.08 in ps previous set.
Mean is -2.02

We believe this is Cl which is @ -2.10
so your error here is .08
which is also not good. but it is what you have.

Next we have -1.65
We never had that before either.
Could be Mn
but Al is -1.66 which is more likely
It says that we may have some Contamination.

We have a peak @ -.81
This matches Cl again, good.
Last time we had +.81

We also have a +.65
We did not have that before either.
You must repeat trials until they reproduce!

Chlorine again, Great.
3 Matches in Chlorine.
No Potassium however.
And possible Al Contamination.

The first lesson here is that you must repeat until you have reproducibility and error estimate.

Repeating reference trial & Carpenter Trial:

On reference distilled water trial, I obviously had a major error or contamination. Your magnitude is a fraction of what it was on the first trial. Major check contamination

Watch for overloads! Sometimes you need only 1 drop of a very dilute solution! You never want overload!

This paints a different picture

We now have 2 sets of data on the Carpenteria Crystal. We believe set 2 is the better set

$\bar{X}$	Trial 1		Trial 2
-2.815	-2.92	Ca, Sr, Ba, K	-2.81
	-2.56 No match		No lanthanum match
-2.265	-2.27	H_2	-2.26
	+.76 No match		No iron match
	+1.00 No match		
		Li, Co, N_2, H_2O_2	-1.81
		NO, NO_2, SO_4(.93)	-1.06
		U, Ga, ClO_2, Cl^-	+.63
		H_2O, OH^- O_2, Cl^-	+1.23

This makes sense. It suggests a Chloride salt should be investigated. Remember K was not detected in the control run.

$CaCl_2$ Fails solubility in ethanol & acetone

$SrCl_2$ Fails flame test, fails ethanol, acetone solubility

$BaCl_2$ Fails methanol solubility, flame test

KCl we already know that there is a difference here, but still possible

Potassium Chloride still remains the most viable candidate

Chloride ion test

1. Add dilute nitric acid
2. Add Silver nitrate

OK Carpentaria Crystal passes the Chloride test!

Good Work!

Everything says that it is Potassium Chloride

For some reason, potassium is barely detected in this case but not in my control case. No idea why.

It actually does seem pretty pure.

Sep 05 2016

A great Calorimeter has been made.
This should be far superior.

Our first step is to determine the specific heat for the smaller pipe cap.

Initial temp of lead cap is that of boiling water.
This is = ~~97.2°C~~ Steady. 97.3°C

Calorimeter is filled with water w/ temp = 20.3°C
22.2

You need the mass of the water 341gms

and the lead cap. = 80gms   80.0gms meas and avg w/ 2 scales

$Q = M_p C_p \Delta T_p$ $Q_w = M_w C_w \Delta T_w$

$Q_p = Q_w$

$m_p C_p \Delta T_p = M_w C_w \Delta T_w$

$$C_p = \frac{M_w C_w \Delta T_w}{m_p \Delta T_p} = \frac{(341\text{gms})\overset{\text{J/gm.C}}{(4.184)}(22.2-20.3)}{(80\text{gms})(100-22.2)}$$

$= \underline{\underline{0.44}}$ This is much much closer to the theoretical value of 0.49
Maybe not bad. Now check it.

Ok. Do it again.

Mass of water to be used from now on will
be 340 ml = 340 gms

need
Initial temp of water that stabilizes pipe cap 96.2

Initial temp of Calorimeter = ~~20.2~~ 20.3
Final temp of calorimeter = 22.2

Mass of pipe cap = 80.0 gms.

$$c_p = \frac{m_w C_w \Delta T_w}{m_p \Delta T_p}$$

(Cont could be a melting pt)
ΔT_p = Initial water temp in beaker − Final temp of water in calorimeter (because they are equal; pipe = water)

ΔT_w = Change in Calorimeter temp

$$= \frac{\overset{340}{\cancel{80}}(4.184)(\overset{22.3}{\cancel{22.2}}-20.3)}{80(96.2-\underset{22.3}{\cancel{22.2}})}$$

= 0.46 excellent

V.g this Average is therefore ~~0.45~~ 0.48 vs. theoretical 0.49

You have the specific heat of the smaller lead cap now determined.

This does seem to be the more reliable value.

Waited a little longer for the temperature to stabilize @ its maximum. Approx 5 min.

Today lets see if we can melt the
KCl after calibrating w/ NaOH (?)
& Ammonium Sulfate (?)

You can saw the large pipe cap as a cap
for the small pipe cap.

Now see if you can melt Commercial - KCl

You now have a reliable value for $C_p = 0.48$
vs theoretical 0.49. Good work.

Now heat up water for Calorimeter & Commercial KCl

KCl Measurement

Calorimeter Initial =
Calorimeter Final =

340 gms placed in Calorimeter

Calorimeter cools down ~ 1°/5min @ 80°C

It was a good idea.

You have melted the KCl!
But your calorimeter needs to be bigger.
So now I have one that is.

Weight of water added

1081
976
1067
1016

Σ = 4140 vs 340 = 12 times
gms of H_2O

Initial water temp = 18.3
Final water temp 20.6

$$T_{Fp} = \frac{M_w C_w (T_{Fw} - T_0) + M_p C_p T_0}{M_p C_p}$$

$$= \frac{4140(4.184)(20.6 - 18.3) + 80(0.48)(18.3)}{80(.48)}$$

= ~~1095~~. 1056 This is obviously high.
It is supposed to be 1056.

First goal can we half the water and [illegible], or about 2000 ml

Then the question is for some reason is Cp off. I do not know why it should be.

Now to flame test,

The Cp that would work in this case is about 0.65, Is that possible?

using
Test your math on the calibration data :

(should be 96.2

$$T_{Fp} = \frac{340(4.184)(\cancel{96}\ 22.3 - 20.3) + 80(.40)20.3}{80(.40)}$$

$= 94.4$ No, something is wrong. It should be 96.2

Revise the math:

$Q_p = m_p C_p \Delta T_p$ $\qquad Q_W = M_w C_w \Delta T_w$

$Q_p = Q_w$

$m_p C_p \Delta T_p = M_w C_w \Delta T_W$

What do we want? We want ΔT_p
but ΔT_p is defined as initial temp of water, or
melting pt − final temp of water
in the Calorimeter
(this equals the pipe)

Therefore
M.P or Initial water temp = ΔT_p + final temp of water

Therefore

$\Delta T_p = \dfrac{m_w C_w \Delta T_W}{m_p C_p}$ heat flow alone

$$\boxed{\text{M.P (or initial bath temperature)} = \frac{m_w C_w \Delta T_W}{m_p C_p} + \text{final temp of water in Calorimeter}}$$

and this IS different. Therefore

OK Good

$$\text{mp (or bath temp)} = \frac{340(4.184)(22.3-20.3)}{80\cdot(0.48)} + 22.3$$

$$= 74.1 + 22.3 = 96.4$$

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So our solution for KCl is actually

$$MP = \left[\frac{4140(4.184)(20.6-18.3)}{80(.48)}\right] + 20.6$$

$= 1058.1$ (almost the same as before and too high. We must repeat to the point of stability. Flame heat is not worthy.

Use 2000 ml of water ~~instead~~.

$m_w = 2000$ gms

Initial Water Temp = 18.1

Final Water Temp = 21.7

$$MP = \frac{(2000)(4.184)(21.7-18.1)}{80(.48)} + 18.1 = \underline{\underline{803^\circ}}$$

Not bad!

We have done it. Actual value is 770°C

Error is 4.2%

If you were to use $C_p = 0.49$ your answer is 787°

Error = 2.2% So this is even better

Use it. $C_p = \underline{0.49}$

Using $C_p = .50$ (also acceptable and perfectly understandable).

Ok, lets go for it. Use the same protocol

Now for Carpenteria Crystal

Temp of Initial water = ~~30.0~~ ~~27.5~~ ~~28.0~~ ~~27.8~~ ~~27.7~~ ~~27.6~~ 27.5

Final Temp of Water = 31.1

~~AR~~ MP of Carpenteria:

$$= \frac{2000(4.184)(31.1-27.5)}{80(.5)} + 27.5$$

= ~~780~~ 781°C

vs actual is ~~780~~ 770

Error = 1.4% Excellent work

Rule of Thumb Seems to be

Volume of Calorimeter ≅ 2.5 times the MP Temperature

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[redacted]

We have

1. Melting point by Calorimetry
2. Electrolysis Combined w/ solubility tests
3. Cubic crystal form
4. Chloride ion test (w/ electrolysis)
5. Density estimate
6. Appearance under scope

I need MPs for — soluble in ~~methanol~~ alcohols, density too low

Soluble in ethanol $CaCl_2$ 772 orthorhombic, tetragonal, trigonal — fails solubility test in ethanol & acetone

$SrCl_2$ 874

$BaCl_2$ 962

* insoluble in ethanol KCl 770

Lanthanum Chloride MP is 858°C so no.

$LiCl$ 605°

$CsCl$ 645

~~SiCl No such thing~~

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We have worked very hard on the Carpinteria Crystal question. We seem to have come to a consensus on the nature of the material. The assessment is one primarily of potassium chloride.

Your decision is based upon:

None of these are fatal flaws, mixture is a possible explanation

What Works	What Doesn't Work
Electrochemistry Candidate $CaCl_2$ absorbs moisture from air	Group I & II not unique
Solubility Tests - Full Agreement glycol, alcohol, water	No problems
Melting Point Determination	No problems But mixture is indicated
Density estimate	In agreement
	Flame test - Both Control & Sample
Cubic Crystals under scope	Other crystal structural types also visible, even in the majority.
Chloride is verified by Electrochemistry & [illegible]	There are many chlorides
Conductivity?	Consistent
pH?	No such thing as pH of a salt, no fit
IOR?	Cons[illegible] length

Sep 06 2016

We have an interesting observation on the COB culture in incubated test tubes. They are producing a reddish layer of solution @ the top of the solution after several days of age. What is this reddish layer? Is it iron?
How are you going to analyze the layer?
Electro Chemistry?

Sep 09 2016

Calibrated Conductivity ~~Testy~~

KCl Control solution 0.10 gms

Beaker 34.75 gms

34.97 w/ KCl

$\Delta =$ 0.22 gms

Total w/ water = 86.95 gms
- .0.22 gms KCl
86.73 water + beaker
- 34.75
51.98 ml H_2O = 51.98 gm H_2O

MW of KCl is: 74.55 gms
Assuming unhydrated form our solution is therefore

$\underline{0.22}$ gms

$$1M = \frac{74.55 \text{ gms}}{1000 \text{ ml}} = k\left(\frac{0.22}{51.98 \text{ ml}}\right)$$

$k = .0042$

So we have a .0042M solution

$$\frac{.3155 \text{ gms}}{1000 \text{ ml}} = \frac{x}{51.98}$$

$x =$

$$\frac{0.22}{74.55}\left(\cancel{74.55}\right) = \frac{.00295M}{1000 \text{ gm}}$$

but we have 51.98ml so $\frac{1000}{51.98} = 19.238$

and $19.238(.00295M) =$

$= \underline{.057M}$

Call straight talk tomorrow.

A simple example of a redox reaction is adding FeSO$_4$ (+2) to bleach.
Initial ORP of 1 drop of bleach is 694 mV.
It drops to 0350 w/ the addition of some iron.

0000 The ORP meter clearly measures the state
Sep 10 of oxidation of the culture medium
= ~ 300 before culture introduction.
Culture introduction causes a rise of ORP to
~ 340 mV.

Conductivity of initial culture = 2.71 mS.

[Conductivity of a mature culture is 9.70 mS
ORP of a mature culture is 282 mV]

This suggests that the culture might increase conductivity and decrease ORP?

	Young Culture	Mature Culture
Conductivity	2.71 mS	9.70 mS
ORP	340 mV	280 mV

Not necessarily the right concentration —

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	Time	EC	ORP
Sep [illegible] 08	0000	2.71 ms	340 mV
	~~1330~~ 0130	2.89	362
	~~1445~~ 0245	2.89	350
	1100	2.89 ~~2.88~~ ~~2.86~~	~~284~~ 286

We notice that our cultures that are several days old under incubation form a red layer on the top. What is this?

Sep 09 2016

ORP Study

You are getting very interesting results already w.r.t. ORP measurements

Differential measurements relative to a blank actually seem to be the most practical.

It is amazing but distilled waters are varying amongst themselves considerably.

Wallace tap water seems to be coming out amazingly on zero, or of a reducing nature

$FeSO_4$ & urine are reducing.
Bleach is incredibly oxidizing
Vit C & Sugars are uncertain as they are measuring positive even though they are stated to be reducers (have seen Vit C)
Culture in Urine Urine, sugar, $FeSO_4$ & H_2O_2 are quite sensible now.

– Wallace water came out @ 0001 mV!
\+ Distilled CO came out @ +90mV / Wal
– Wal +38 rel to CO
GreenTea +52 relative to Wal +38
So you see that change is what is important

You can see that differentials relative to a blank or standard are what matters.

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Let Wallace tap = 0.0.

Co Distilled = +90   Δ=+90

Wal Distilled vs CO Distilled = +38
So 38-90 = Δ-52

Wallace: (0 → 90)   (90 → 38) Co
to CO   +90   -52   to Wallace

Time is a factor here

0   38
X=+19 for Wallace

+90 for Co Distilled

Green Tea is 46
46-19 = +27 for Green Tea
Wal
X

For Culture w/
~~Ur~~ Urine
FeSO4
Sugar
H_2O_2
+CDB

We have a massive precipitate forming

3mm

2nd Run

1. Rinse terminals between Tests
2. Strongly oxidizing solutions (eg bleach) must be neutralized w/ strong reducer (eg FeSO4 + urine)

Wallace: +19, +16, 0

Co Distilled: +90

Green Tea: + 27

Urine : ~~+16~~ +12

FeSO4 : +70

Notice how hard to come by.

Urine + FeSO4 : -120 (highly reducing), -150

1 drop Bleach in 50 ml: +585

Vit C ~~+104~~

Glucose Tablet +85

NAC +97

This mean good reference solution to have on hand are Co Distilled & FeSO4-Urine

The more extreme the measurement is (eg, bleach) the longer the meter requires to reach an equilibrium in reversal.
Eg after bleach, it takes about 1/2 hr to return to ~-150 in Urine and FeSO4.

I now have an idea of what ORP actually entails. I can also understand how hard it is to find a reducer that can be consumed in the body

Note:

I think your meter actually was off. Turning the POT clockwise actually decrease the reading, not increase it!

It looks like maybe you cannot calibrate it near zero.

I can see that this is true.
You seem to need to calibrate it at the more extreme value.

Urine + Fe SO_4: I ultimate ~~+25~~ -250mV

Bleach (50ml H_2O / 1 ~~[illegible]~~ 1 drop)

Bleach is now going up to +1100.
Interesting.
It seems to widen the range as opposed to offset the zero point.

I think the pot is decreasing the range, not offsetting the zero point.

Bleach is extreme so it takes a long time to restabilize.

Sep 09 2016

We have modified the mod size calorimeter so that it will handle up to 800°C by using a smaller cup! We also have received our melting block!

NaCl test:

~~19.3~~°C H_2O initial ~~19.4~~ ~~19.5~~ 19.6
H_2O Final 34.5°C

We have also learned that ~ 3 ml of 340 ml initial volume is lost in steam @ 800°C. This is adjusted for by filling to 343 ml.

Steel Cup 3/8 weighs ~ 35gms. instead of Ex

The new calorimeter working great!
However adding the metal plate means that some of the heat is absorbed by the steel cup. Leave the water alone @ 340 ml in the comps.

However 6 ml of water was lost again through steam and weighing. We estimate 4 ml actual loss.

The mass of the stainless steel cup is 18.0 gms
Specific heat of stainless steel is essentially the same as 0.50

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What this actually means though is that we have

340 ml H_2O = 340 gm.
− 4 ml anticipated loss @ 800°C
+18 gms stainless steel cup w/ same C_p

So our actual mass [@ 800°C]! is 354 gms

that is heating up.

So estimated MP for NaCl is:

$$MP = \frac{m_w C_w \Delta T_w}{m_p C_p} + T_{\text{water final in Calorimeter}}$$

$m_w = 354$ gms
$C_w = 4.184$
$\Delta T_w = (34.5 - 19.6) = 14.90$
$m_p = 36.2$
$C_p = 0.50$
$T_{\text{water final}} = 34.5$

$$MP = \frac{(354)(4.184)\,14.90}{36.2\text{gms}\,(.50)} + 34.5 = 1254$$

OK, we have a problem here. It is 801°C.

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Start by determining Cp.
Something is very wrong here.

Mp actually 36.1
You would need a Cp here of ~ ~~.75~~ 0.80
I am not sure how that is possible.

Let's try ~~sodium~~ ~~ammonium~~ sodium hydroxide (318°C)
NO! It damages & reacts w/ lead

Use Ammonium Sulfate You got it a little too hot.

H_2O initial = 18.6°C
H_2O Final = ~~25.0~~ ~~25.1~~ 25.0

$$MP = \frac{(340)(4.184)(25-18.6)}{\cancel{35}\ 36.0(.80)} + 25.0 = 341°C$$

$169^\circ 6^\circ C$

169 Would be the top of the melting block!

Way way too high.
Repeat.

NaCl again.
Water Initial = 19.2°C
Water Final = 34.35

$$\frac{340(4.184)(34.35-19.2)}{(36gms)(.80)} + 34.35 = \cancel{782}\ 783^\circ$$

vs 801° Error = 2.2% This is excellent still.
We could use 354 gms.
= 813 $\bar{x} = 798$

This mean we'll want to, up the stainless cup.

Use

$M_w = \underline{347}$ gms w/water filled to 340 ml.

$M_p = 36.0$ gms.

$C_p = \underline{0.80}$ I do not know why it is this high but it is.

Let's try manganese sulfate.

T_w Initial 17.6°C
32.0

It could indeed be that you let the get too hot.

$$MP \cong \frac{(347)(4.184)(32-17.6)}{36.0(.80)} + 32$$

$= 758$ Actual is 710

I do agree that it got this too hot.

O.K. what you really have is

$$\frac{340\,gm(4.184) + 18\,gms(.5)}{4.184 + .5} =$$

$\underline{358\,gms}\,(4.00)$ ✓

So what we really have is with ~~the~~ combined Stainless cup

Mw = 35~~0~~8 gms - loss
we can estimate that @ 3 ml

or

Mw = 355 gms
with Cw = 4.00 modified.

So let go back to salt NaCl

New Cp

~~[illegible]~~ 34.5

$$\frac{355\,(4.0)(14.90)}{36\,(x)} = \text{~~801~~}°C \qquad x = \text{~~[illegible]~~}\ \boxed{0.77}\ \text{Case 1}$$

798°C

Case 2:

34.35 ~~29~~ − 19.2

$$\frac{355\,(4.0)(\cancel{32 - 17.6})}{0.77\,(36)} + 32 = 808$$

x = 803

Actual = 801 Error = 0.25%

OK, you have it.

Mw with 340 ml + Metal Cap = 355 gms
Cw (modified w/ cap) = 4.00
Mp = 36.0 gms
Cp = 0.77 calibrated w/ NaCl.

Now we can apply this to $MnSO_4$
but realizing we got it too hot

$$\hat{MP} = \frac{355(4.00)}{36(.77)}(32-17.6) + 32^\circ C$$

$$= 770^\circ C$$ but actual is 710°C

you did get it too hot

Would you like to try again. $MnSO_4$

$M_w = 355$ gms (340 ml + cap)
T_w (initial) = ~~18.1~~ ~~18.0~~ 18.1 18.3
T_w (final) = 30.3

$$MP = \frac{355(4.00)}{36(.77)}(30.3-18.3) + 30.3$$

$$= 645$$ But actual is 710°C

The method seemed sound, this time.
If $C_p = .75$ MP = 660 That is a big difference from before?

You may need to do this again. The chance it was not hot enough:

$$\frac{645 + 770}{2} = 708$$

which is surprisingly close.

I think you need to try KCl
Actual is 710°C

(amazingly close averaging) I think you need to leave your parameters alone & take averages.

Our solution is therefore .057M of KCl

And the conductivity measured is: 7.15 mS

Now to CC crystal

Wgt of beaker = 34.91 gms

Beaker + CC = 35.13

Beaker + CC + H_2O = 88.71 gms

Therefore ΔCC = 0.22 gms

Assuming it is KCl our M solution will be

$$\begin{array}{r} 88.71 \\ -\ 0.22 \\ -\ 34.91 \\ \hline = 53.58\text{ ml} \end{array}$$

$\frac{.22\text{gms}}{74.55}$ = .00295M if it were 1000 ml. But it is not. It is 53.58ml

$\frac{1000}{53.58} = 18.664$

So 18.664(.00295M) = .055M Hypothetical KCl

So $\frac{.055}{.057}$(7.15mS) = 6.90 mS anticipated

Error = 0.6%

We measure 6.94 mS

Excellent

We have a match.

Now on
1. Voltammetry
2. Density
3. Melting Point
4. Cubic Crystal
5. Chloride Ion Test
6. Appearance / Microscope
7. Conductivity
8. Solubility Tests

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This shows you that you should not be dismissing your measurements. Some material may be easier to determine than other.

1. Examine urine based culture
2. Examine HEPA filter

Sep 10 2016

Many many questions as usual?

1. Does urine-sugar w/out CDB produce hydrocarbons? They are of no value

2. Are hydrocarbons produced by the CDB? w/a urine culture? If so, which ones? They all seem very iffy except for CO_2 H_2 & CO.

3. What is the significance of thioglycol or dithioglycol? It is created by the CDB.

* 4. Can Lanthanum precipitate phosphate from the rainwater?

5. Do the CDB proteins dissolve in methanol? Only very slightly, but some specific IR from it

6. Can urine be placed into the GC? Yes! I have detected urea!

* 7. What are the solids in the HEPA filter? Are they amenable to IR? What about microscopy? This does seem to be a problem. Electrochemistry is the <u>best</u>.

8. Can you develop a method to monitor the culture electrochemically? Small Test tube, electrodes? Conducting meter?

The urine-sugar-Fe medium WITHOUT CDB also is producing ethane so there is nothing unique here. Assuming that this is ethane and not CO_2 which makes it even less unique. There is no strong sign of CO_2 production by any urine-sugar culture so this casts doubt as to its viability as a medium.

—

The HEPA filter matches the rainfall.

The HEPA filter matches the CDB Protein Complex

The HEPA filter has a reasonably close match
with: Decanoic Acid
2 acetyl ~~ethe~~ ethyl ester

This is an important discovery.

What is a solvent that will leave a clean peak? Pure Xylene

You are answering some of your questions today.

1. The urine-CDB cultures appear to be a complete bust

2. The red test tube layer from CDB is a new compound to be explored.

3. Plastics (phthalates) come from the end product CDB

4. Capric acid (decanoic acid) is coming from HEPA & rainwater. This is found in butter and coconut oil. It is C_{10}, only to be found in animal and some plant fats. It is a fatty acid. It is not supposed to be in bacteria. Caproic Acid (C_6) is, but it is within LPS.

5. Solid analysis of HEPA did not go well yet. Maybe microwave?

6. ZnSe crystal? Acids, bases?
Only (6.5 - 9.5 pH) No bases either!

Very mild base is OK No, not so good

7. We are learning quite a few structural details and overlap between HEPA, rain, & CDB.

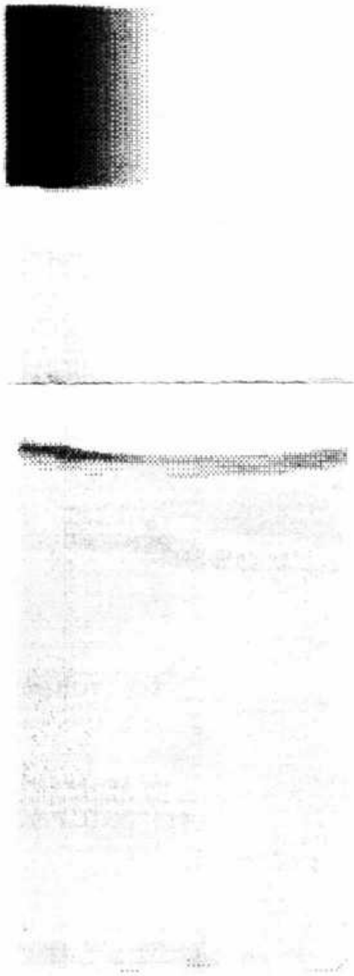
Urine has 95% water

I believe that we have detected an identified our first "contaminants" in a solvent. i.e., urea in water, ie, urine. We get an area of 1.7% which is quite in keeping w/ the chart.

Everything else is inorganic & non volatile except ammonia?

The melting point of urea (which is a solid that is highly soluble in water) is 133°C. so that is very low. How would you detect ammonia?

We are therefore detecting urea. This would be very interesting to try and trap w/ GC.



Urine

0.05% Ammonia
0.18% Sulphate
0.12% Phosphate
0.6% Chloride
0.01% Magnesium
0.015% Calcium
0.6% Potassium
0.1% Sodium
0.1% Creatinine
0.03% Uric acid
2% Urea

95% Water

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You could probably collect mainly
evaporate urine. But man, does
it stink.

What else is urea soluble in?
Can we extract it?

It is only slightly soluble in ethanol.

What about methanol? 1/6 as much as
much as water ~~and ethanol~~.

It does seem highly soluble in methanol (166 gms/l)

"Boiling urine causes irreparable stench damage
to a home!"

Ok, what is really good here is that I have
detected something soluble in a solvent, ie
Urea w/in water. This is great.

Water is always problematic in the GC and it takes a
long time to clean out.

In strongly basic, the PO_4^{3-} predominates

You solved the problem! pH matters.

add 1M KOH to the solution prior to adding $LaCl_3$!

Phosphate Testing

We have a very interesting development with phosphate testing. It should be, without doubt lanthanum chloride ~~that~~ I have received.

It is strange. La^{+3} $Cl^{\cancel{3}-1}$ $LaCl_3$

LaCl yes

My goodness we have PO_3^{3-}

PO_4^{3-}

So we must be forming Lanthanum Phosphate

HPO_4^{2-}

$H_2PO_4^-$

It is $LaPO_4 \cdot x H_2O$

This means that it is only binding w/ PO_4^{3-}

Not PO_3^{3-}

Not HPO_4^{2-}

Not $H_2PO_4^-$

So lanthanum chloride is restricted to a particular form of the phosphate ion. But there are four incarnations of the phosphate ion!

We tested with $\overset{+1}{Na}\overset{+2}{H_2}\overset{-3}{PO_4}$ OK that is why it worked.

We also have $\overset{+2}{Na_2}\overset{+1}{H}\overset{-3}{PO_4}$ it would work also

but PO_3^- HPO_4^{2-} $H_2PO_4^-$ would not work!

in weakly basic forms the HPO_4^{2-} predominates.

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The pH of the solution determine what form of phosphate ion is present

Strongly acidic	H_3PO_4
Weakly acidic	$H_2PO_4^-$
Strongly basic	PO_4^{3-}
Weakly basic	HPO_4^{2-}

This is the nature of the issue.
Solution: Drive the solution to strongly basic so that PO_4^{3-} forms

Then add $LaCl_3$.

We know from this now that our rainwater probably has a mix of HPO_4^{2-} and $H_2PO_4^-$

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$$

When you tested phosphoric acid, it was a highly acidic solution so it did not work there either just like the rain water. But add KOH and it will work!

Sep 11 2016

We made some good progress yesterday with a series of isolated but important events. You are starting to run out of time in the lab.

Some questions on your mind are

1. Rainfall metals - we actually did make an analysis already. You have many controls you can work on a private trip to develop techniques. Between electrochemistry, TLC and fundamental physical properties & polarimetry you should have all that you need for the winter.

In addition, you will have five ideas.

1.
2. [redacted]

Let's move on to next set:

1. Env. filament is rather important I would say. Both organic and inorganic.
2. How do you get an acid/base aqueous sample into ATR?
3. What is the next example of something to analyze by GC
4. Headspace + vacuum improvement?
5. Ester or ether into GC next? What is an ester or an ether for? What are its properties?

Electrochemistry has no problem w/ acid base solutions but IR does!

We are restricted to pH 5-9 w/ ATR

Also no oxidizers like Bleach!

Also no ammonia, no EDTA

What if you were to heat it in methanol instead?
What if you were to transfer it to methanol?
Use Hair as an example.

But methanol is not that polar enough to separate. MET Xylene?

Your hair experiment did not exactly go as smooth as you would like.

You have a good system of breaking down the hair now w/ strong base and the microwave @ moderate heat ie power setting of 3 for ~ 5 minutes.

But you do have a problem in getting out of the strong acid-base mode, which you can not use for ATR.

What happens if you neutralize the base?

Okay, the answer (at least some times) to the strong acid-base ATR problem is to NEUTRALIZE the acid.

This will create water and a salt, which is fine.

It seems to have worked perfectly w/ hair.

This method could apply to many solids. Microwave digestion w/ a strong acid or base and then neutralize.

I am learning how to prepare a hair sample. Could be both IR & GC.

1. Microwave hair in strong KOH w/ moderate power until it dissolves in water.
2. Filter it (double)
3. Dry the solution to residual level gradually, ie, evaporate all water on a watch glass.
4. See if the remaining solids will dissolve in methanol or ethyl acetate or acetone or some polar solvent. (volatile)

Pyrolysis is another plan. IR Pyrolysis may be a lot easier

If proteins precipitate out @ neutral pH then this method does not work.

Your hair sample is looking very good.
It is drying in a crystal or a powder.

It is interesting but the finest hair powder in the world is doing nothing in IR ATR.
I am not sure why but it is doing nothing.

We have success now w/ a level of extraction
the acetone extraction (and methanol washing).
Layered film of acetone extract on ATR is working.

The acetone or methanol extract has a definite pink color to it. This is unusual. Maybe NIR is useful also. Maybe GC is useful also
Maybe VIS is useful also. UV would be if I had it.
I have succeeded. It took a lot of work but it is worth it.

Methanol & acetone work w/ the dried powder to produce the pink solution. Film on IR ATR works.

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Sep 12 2016

Another exciting day for Clifford!

1. Photograph the red felt tube layer
2. Digest large sample hair [redacted]
3. Screen shot [redacted]

4. Apply hair methods developed to the Env. Filament.
5. Repeat GC w/ ethyl acetate
6. Another GC experiment w/something dissolved
   (must be volatile)

7. Look @ TLC books

8. Other major projects before winter still included

   1. DNA Electrophoresis
   2. Protein Study - Electrophoresis

9. We are looking @ our list of May 31 2016
and evaluating it. We have done fairly well.

The List of May 31 2016 was:	Progress Report: Sep 12 2016
1. DNA Work	NONE
2. Env Filament Work	Initial Progress Electrochemistry, Digestion
3. CDB, Protein & Lipids Work	Some Progress, Overlap w/ Env. Samples, Distillation Progress
4. Write up rainfall studies	Additional Findings, Biological, Organic
5. IR Recovery	Very Good w/ Search Capability now & DB available
6. Electrophoresis	NONE
[redacted] Book	[redacted] OK!
8. Hair Analysis, IR & GC	Digestion Progress, Initial Organic IR Work
9. Urine Analysis IR & GC	GC Analysis is Favorable
10. GC Skill Development, Application	Model Development, Urea, Esters, Ketones, Ethers, Polarity, Porapak
11. Davis, Organic Chemistry	Very Little
12. Citizen Samples	Generally good, Two Primary Samples
13. HEPA Filter Analysis	Good Solvent work, IR Biologicals Still need electrochemistry
14. Distillation Studies	Very good work here
15. Pyrolysis & Headspace Study	Pyrolysis good work, Headspace remains

We have generally done fairly well

What we're organizing now are (in the lab)

Lab

1. Digestion Hair Analysis
2. Env Filament Digestion Analysis
3. HEPA Electrochemistry
4. Headspace Study
5. GC: Ketones, Esters, Ethers, COOH
6. Electrophoresis - DNA?
7. Protein Analysis
   CDB - Milk, General
8. TLC Prep

Field

1. Supplement Paper
2. Rainfall Paper
3. Analyze IR
4. Analyze GC
5. Electrochemistry
   Galvanic & Impedance
6. Physiochemical Properties
   MP, BP, IOR, Density, pH
   σ, TDS, ORP, ~~% Carbon~~
7. Polarimetry
8. UV-VIS
9. % Carbon
10. RLC, Oscilloscope
11. TLC!
12. Paper Chromatography!
13. Paper Electrophoresis!
14. Refractometer

Let's work w/ a Naptha headspace problem.
It looks perfect, C7 - C15
w/ Cyclic Compounds. A good Combination.

Lets setup headspace
& then Compare to IR,

—

For Hair Digestion

1. Microwave of Conc lye modestly & steadily
2. Neutralize the pH!
3. Evaporate in glass @ 60°C
4. Powder the sample
5. Consider solvents such as acetone, ethanol, methanol (NO WATER)

Acetone is most volatile & easiest to use w/ IR
Consider GC also.

—

We have learned that you do not want to be heating in boiling lye & pyrolyzing hair.

—

You are doing some very good sample prep. You now have about 15 ml of very pure finely powdered hair sample. You are learning that a fine powder in solution, even if not entirely dissolved, can still make a fine filming layer for IR & ATR if placed on & evaporating solvent.

Sep 13 2016

A potentially important finding. Hair is testing positive for phosphates present. I do not see evidence yet they should be there along w/ 15'ganide

The thesis does not make a single reference to phosphorus in hair 365 page analysis.

Level of phosphorus in both [redacted] appear to be the same.

Phosphorus is definitely in hair.

Sep 15 2016

In hair, the weak peak @ ~ 2150 is not cyanide.

It IS an alkene!

ATR Blood Prep

Also, we have learned how to IR Blood on the ATR properly.

1. Put a drop of blood on the ATR.
2. Put on the slide and let it set, maybe up to a half hour while it slowly coagulates.
3. Remove the slide w/out scratching the crystal surface.
4. The blood will then dry into a thin film that gives a good ATR plot.

Otherwise the blood never dries or is too thin or thick and it is dominated by water or too thick for a good ATR sample. You are getting good results now.

Believe it or not, the closest match to the blood sample is the Env. Filament project average of KCl & ATR work combined July 05 2015.

VIS - NIR Work.

The CDB are producing an reddish colored alcohol. This implies a transition metal, most likely, combined w/ an alcohol.

We also have (it needs to be confirmed) ethane production by the CDB per GC.
This is only @ 150°C. This must be Confirmed by Control runs.

We are after:

1. Hair   Urine?
2. Blood
3. Saliva
4. The "Red layer"

We have an alkene-iron-alcohol combination - doesn't sound good

We are making progress in each. The common thread seems to be alkynes. These can be tested and they are highly reactive. Potassium Permanganate

!!! We get a very positive test for alkynes with the CDB red layer + yellow.

Yellow means an unsaturated hydrocarbon NOT aromatic

W/blood we get reddish brown. A major red brown precipitate is formed in blood.

$KMnO_4$ tests are being passed w/ both blood & culture development.

Culture development for alcohol & alkynes
Blood for alkynes

IR & $KMnO_4$ tests both pass.

Blood is testing positive for alkenes (or) alkynes
Brown

w/ $KMnO_4$ Red layer is testing positive for alkynes.
Yellow

Dilute
Acid solution turns colorless.
Slightly alkaline turns brown

so acidic is best YES!

Ok stop the presses.

Both Blood and the CDB Red layer formation test positive for the presence of alkynes by both IR & Baeyer Test.
~~To~~
(uses acid + Potessium Permanganate)
Acid method is better since it turns the solution clear, even with blood.

Therefore in acidic conditions for both:

The CDB Baeyer test turn the solution from red to ~~Clear~~ yellow with the addition of several drops of $KMnO_4$.

The blood turns clear after several micro drops of $KMnO_4$.

1. Use about 2-3 ml of water.
2. a few small drops of blood from a finger prick (turns light red)
3. add micro drops of $KMnO_4$. It will turn progressively clear.

This is potentially very important.

Alkynes in both blood & the culture.

You need to study alkenes in <u>detail</u>.

Alcohol] Ritter Reaction (?)
Alkynes]
From
Acid

1. Polymerization of ~~alkenes~~ alkyne w/ acid

2. ~~Alkenes~~ Alkyne an

Sep 16 2016

Our polarimeter arrived today!

It is a little larger than I thought it might be. Could be a little tricky to bring on our trip but I think that it is possible

We put some sugar in 100 ml and we measure 1.15° degrees rotation.

$1.15^\circ = 100z \quad z = .0115$

$T = 2{,}880 \cdot z = .0331\%$ ~~stat~~ solution.

$\alpha = \frac{\alpha_{obs}}{C \cdot l}$

l in decimeters cell length not volume

C = gms/ml

α = specific rotation

α obs

n

$C = \frac{\alpha_{obs}}{\alpha \cdot l} = \frac{1.15^\circ}{\alpha \cdot \frac{10}{10}} = \frac{1.15^\circ}{\alpha \cdot (1)}$

$\alpha = 64.5^\circ$

so $C = \frac{1.15^\circ}{64.5^\circ} = .018$ gms/ml

Since 1 ml = 1 gm $= \frac{.018\text{ gms}}{1\text{ gms}} \quad \frac{x}{1E6\text{ gms}} \quad x = 18{,}000$ PPM

So you can weigh it and check easily $= \frac{1.8\text{ gms}}{100\text{ ml}}$

Dr Now lets measure:

Our concentration is
$\frac{0.45 \text{ gms table sugar}}{100 \text{ ml}}$

0.45 gms

$100 - .45 = 99.55$ ml

measure 0.5°

$$C = \frac{\alpha_{obs}}{\alpha \cdot (1.0)} = \frac{0.5^\circ}{64.5^\circ} = .00775 \text{ gms/ml}$$

$= 0.775$ gms/100ml

Well it is off but maybe it is tolerable?

It is sucrose. So what is the error? from?

Now we measure 0.30°
This leads to

$$C = \frac{0.30^\circ}{64.5(1)} = .00465 \text{ gms/ ml}$$

$= .465$ gms / 100 ml

vs 0.45 grams

Excellent work.

Apparently the lamp had to warm up further or the solution had to completely dissolve.

Either way, you did it perfectly!

Great Job.

you might need to fill the [illegible] vial to the very tip.

Now we fill the vial the entire way.
We measure:

We end up measuring from .2 - .45°

that gives an avg of 0.325°

$$C = \frac{0.325}{64.5(1)} = .005 \text{ gms/ml} = \frac{0.5 \text{ gms}}{100 \text{ ml}}$$

So we are measuring to 0.05 gms / 100 ml
This is quite good. = 50 mg per 100 ml

All is working well.

Ones red-flask take layer

We have optical rotation of

0.1° ~~-0.5~~ -.05

0.0° ~~±.5~~ .15 $\bar{x} = \pm.05$

0.1° ~~+.5~~ .15

0.0° ~~-.05~~ ±.05

Therefore Concentration is so low as to not to be detectable or it is not Chiral,