Indian Institute of Technology Madras

NPTEL
National Programme on Technology Enhanced Learning

Chemical Engineering Thermodynamics
By

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Lecture 28

Illustrative Examples III

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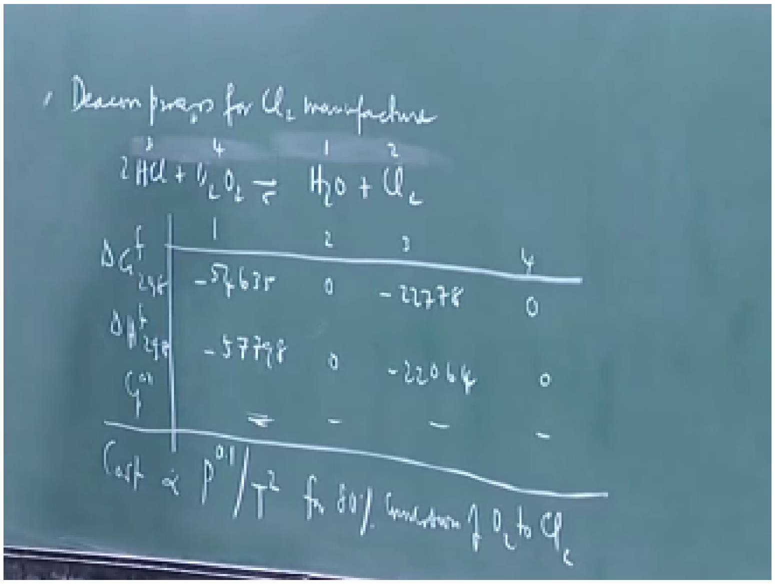

1 Deacon process for Cl_2 manufacture

$$\overset{3}{2HCl} + \overset{4}{\tfrac{1}{2}O_2} \rightleftharpoons \overset{1}{H_2O} + \overset{2}{Cl_2}$$

	1	2	3	4
ΔG^f_{298}	-57635	0	-22778	0
ΔH^f_{298}	-57798	0	-22064	0
C_p^{av}	–	–	–	–

Cost $\propto P^{0.1}/T^2$ for 80% conversion of O_2 to Cl_2

Just maybe part of your assignment problem also, first one is this a decan process in which you have 2Hcl + ½ o2 gives you this is for chlorine manufactures, data is available Δ gf 298 Δ hf 298 is available and cp average available over the range of temperatures this is a we call this 1, 2, 3, and this is 4, 1 this is – 2 is oxygen okay, 3 is water so I have got this mixture sorry the this is 1, 2, 3, 4, or hcl it is -22778 this is -57798 4, 0, I think I leave this cp average you do not need this skip the data the data is not given you is assume Δ cp 0 for the reaction.

Finally there is an another curies information this is typical industrial optimization by t 2 you have do this operation at some temperature and pressure the question is what is the optimum value of temperature at which you should done this reactor. This cost has been this is based on 80% conversion of oxygen to chlorine. Up to this is data first thing is you have to get Δ g as a function of temperature for the reaction.

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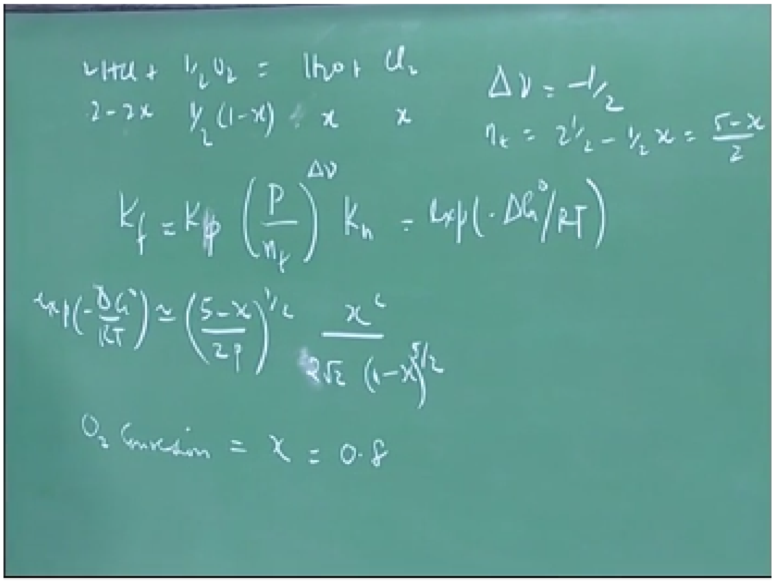

$$2HCl + \tfrac{1}{2}O_2 = 1H_2O + Cl_2$$

$$2-2x \quad \tfrac{1}{2}(1-x) \quad x \quad x$$

$$\Delta\nu = -\tfrac{1}{2}$$

$$n_t = 2\tfrac{1}{2} - \tfrac{1}{2}x = \frac{5-x}{2}$$

$$K_f = K_\phi \left(\frac{P}{n_t}\right)^{\Delta\nu} K_n = \exp(-\Delta G^0/RT)$$

$$\exp\left(-\frac{\Delta G^0}{RT}\right) \simeq \left(\frac{5-x}{2P}\right)^{1/2} \frac{x^2}{2\sqrt{2}\,(1-x)^{5/2}}$$

O_2 Conversion = x = 0.8

So you are looking at basically he reaction formulation simply at equilibrium you are looking at 2-2x this is hcl + ½ oxygen giving you h2o + cl2 2- 2x you start with 2 moles in half a mole ½ x 1 – x and this is x moles this is x moles your kf is simply Kφ times p total moles to the Δ then kn, this of course is equal to the exponential of –Δ g0 / rt. This cost that they have worked out is purely based on operational considerations and they have a compressor they have a heating element they note the cost of energy for heating hence one.

Usually given empirically for a range, so I have this at the moment we will set kφ = 1 this pressure to the power Δ μ is 2 here and 2 and ½, so Δ μ is – ½ it is just the sum over I so it is one and one for water and chlorine in to -2 and – ½ so you get essentially total moles – 2xs – ½ x I have so 2 and a ½ - ½ x or – x / 2, so I have 5 – x / 2p to the power ½ kn is of course x2 / 22 is four this is to the power ½ . √2 or 2 √ 2 x 1- x is to the power 2 it is to the power ½, so this is to the power 5/2.

So I have essentially exponential of –Δ g0 / rt, oxygen conversion is simply x and this case it is the desirable oxygen conversion is given as 0.8 thermodynamic you user some equations in every reaction engineering problem in industry you have some special constrains they will decide how much of conversion they need what is the minimum conversion they will accept, and this is being worked out at 80% conversion this possible that downstream use of chlorine this particular application may have had in a particular plant may require some oxygen to a present to it depends on the application to its final product.

Also they may have found that it is we can also do that calculation you can found that in sun economical the cost increases tremendous they when you try to increase a conversion beyond that, but we can double check that but this is so first you have to find Δ g0 / rt you have to know this functional temperature is equal to some pressure and conversion, so if x is known p becomes a functioning of temperature, so the cost becomes a function of temperature alone that functional temperature differentiated in z = 0 will give the optimal temperature.

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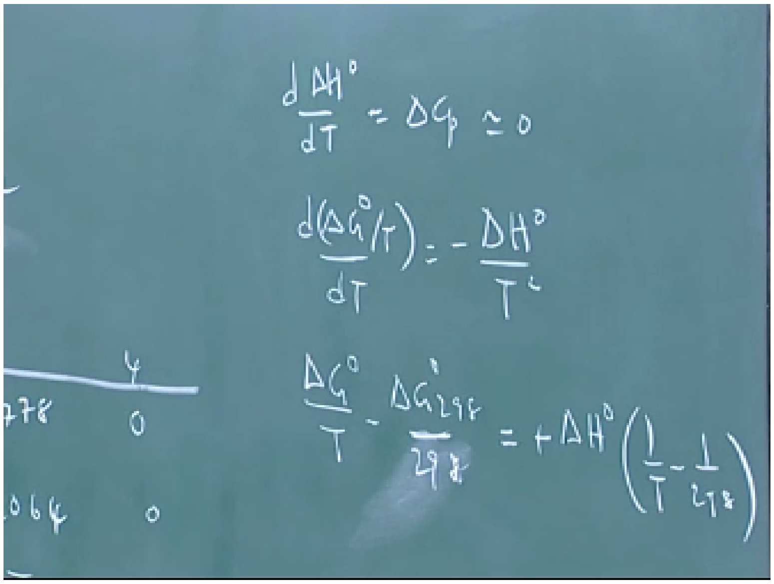

$$\frac{d\Delta H^\circ}{dT} = \Delta C_p \simeq 0$$

$$\frac{d(\Delta G^\circ/T)}{dT} = -\frac{\Delta H^\circ}{T^2}$$

$$\frac{\Delta G^\circ}{T} - \frac{\Delta G^\circ_{298}}{298} = +\Delta H^\circ\left(\frac{1}{T} - \frac{1}{298}\right)$$

If you look at Δ g0, d of Δh0 / dt is Δ cp I am going to take this as 0 then d Δ g0 / t / dt = - Δ h0 / t2 so if integrate this you get Δ g0 / t – Δ g0 298 / 298 I am integrating this over t it will give you – Δh0 which is now a constant or + Δh0 x 1 / t – 1/ 298. My recommendation in reaction engineering is reaction equilibrium calculation, do not simplify these numbers carry them as it is in do the calculation only the last step otherwise you make silly mistakes here and there sometimes they cancel out your unnecessarily calculating this.

Now at this stage you have Δ at 298 first of all Δ h0 you just take this difference you have to take h20 – 2hcl this is $h2_0$ that is 2hcl so it is 57.

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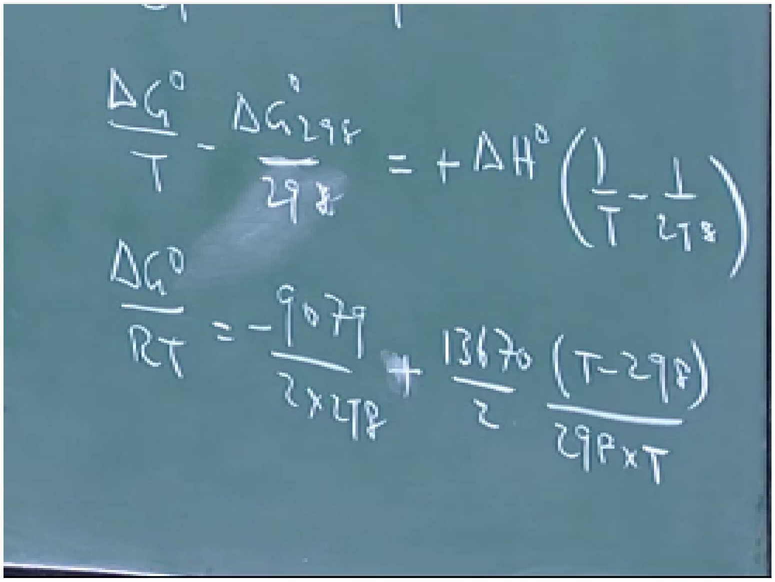

$$\frac{\Delta G^0}{T} - \frac{\Delta G^0_{298}}{298} = +\Delta H^0\left(\frac{1}{T} - \frac{1}{298}\right)$$

$$\frac{\Delta G^0}{RT} = -\frac{9079}{2\times 298} + \frac{13670}{2}\,\frac{(T-298)}{298\times T}$$

This is constant so you get -57798 + 44128 = -13670, and this same at all temperatures, Δ g0 298 it is because Δ cp is 0 otherwise you would have carried it this is – 54635 + 45556, so I need Δg0= / t / rt will give you Δ g0 / r x 2908 I think this is given in all of this calories per gram or, I have note at the unites must be calories per gram you have factor of 2 again do not calculate Δ g0 and then calculate Δg0 / rt again you need only Δ g0 / rt. So Δg0 / rt x 298 this is 9079 / 2 x 298 – Δh0 is – or I will make this + 13670 / 2.

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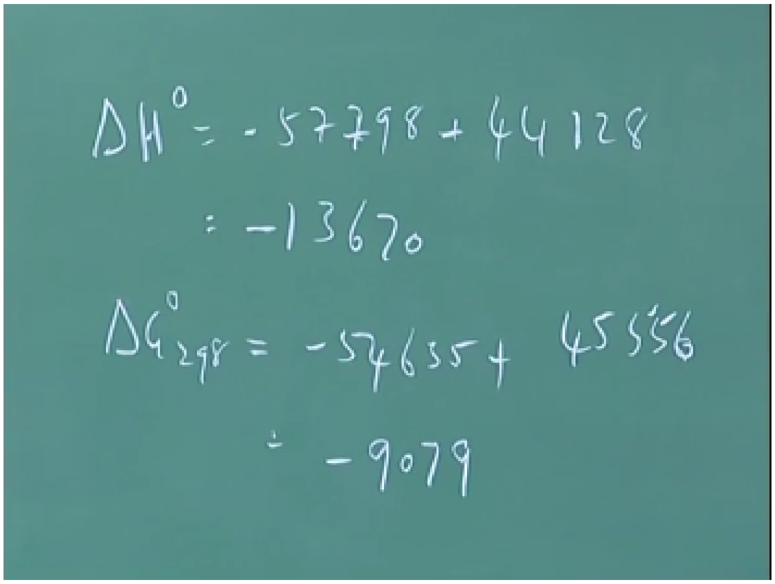

$$\Delta H^0 = -57798 + 44128$$
$$= -13670$$
$$\Delta G^0_{298} = -54635 + 45556$$
$$= -9079$$

This is t – 298 / 298 x t.

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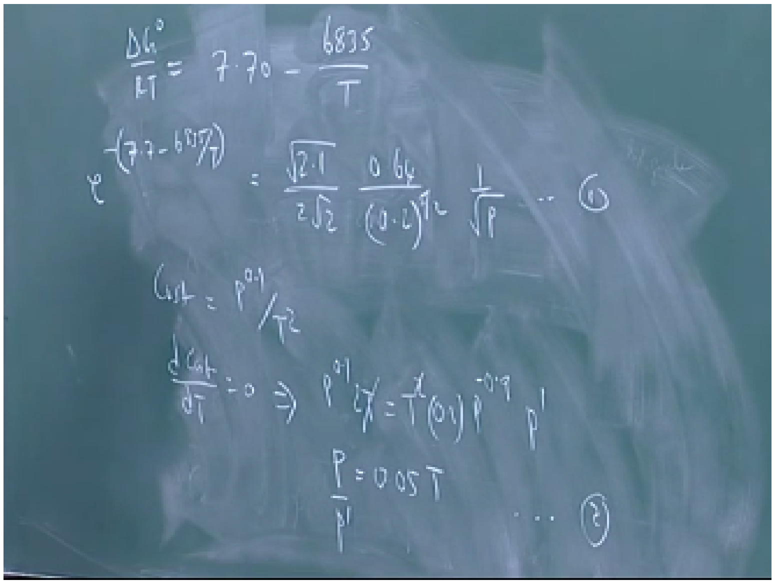

$$\frac{\Delta G^\circ}{RT} = 7.70 - \frac{6835}{T}$$

$$e^{-(7.7-6835/T)} = \frac{\sqrt{2.1}}{2\sqrt{2}}\,\frac{0.64}{(0.2)^{5/2}}\,\frac{1}{\sqrt{P}} \quad \cdots ①$$

$$C_{ost} = P^{0.1}/T^2$$

$$\frac{dC_{ost}}{dT} = 0 \Rightarrow P^{0.1}\,2T = T^2(0.1)\,P^{-0.9}\,P'$$

$$\frac{P}{P'} = 0.05T \quad \cdots ②$$

So Δ g0 / rt = I have this 9079 and this there is something wrong, no this is okay 2 x 298 so this is 13670 – 9079, 4591/ 2 x 298 this is – 13670 / 2 x t what is this equal to 7 okay 7.70 – this is again 6835 / t, so exponential of this or exponential of – of this = 5 – x per ½ x = 0.8 so it is 4.2 / 2 or 2.1 √ 2.1 / √ p then there is a 2 √ 2 in the denominator I put 2 √ 2 here, and x 2 / 1- x so 0.8 2 or 0.64 / 0.2 to the power 5/2 all those are numbers x 1/ √ p.

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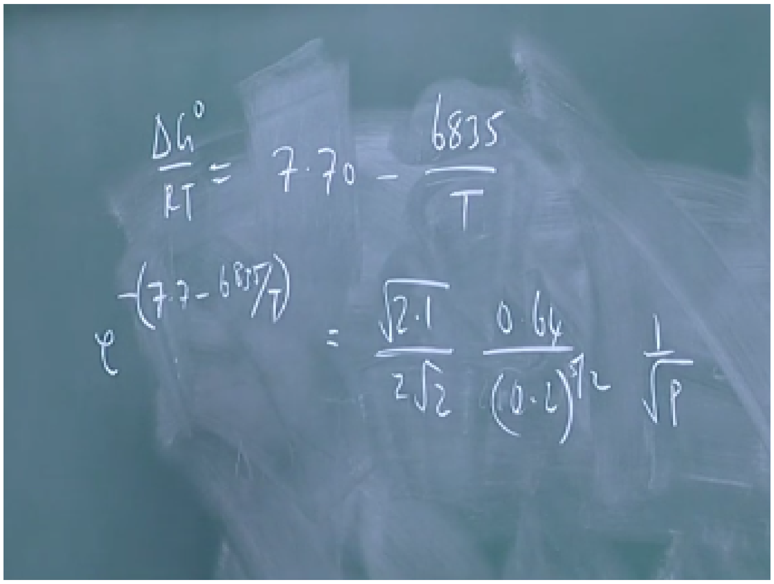

$$\frac{\Delta G^0}{RT} = 7.70 - \frac{6835}{T}$$

$$e^{-(7.7 - 6835/T)} = \frac{\sqrt{2.1}}{2\sqrt{2}} \frac{0.64}{(0.2)^{5/2}} \frac{1}{\sqrt{p}}$$

So finally your cost $p^{0.1}$ / t^2 you have to solve for so d of cost / dt = 0 + $p^{0.1}$ x 2_t = t^2 0.1 $p^{-0.9}$, this t will cancel this is when p if you bring this to the side this is just p p = 0.05 t, this is dp / dt this must be multiplied by dp/ dt p’ so p = p / p’ so you really have to because if you putting this = 0 your saying essentially p’/p = 20/t so that you have to substitute in this, you have to solve these two equations to get t or p whichever you need, you tell me what t comes out to be you do this by trailing error, what you are doing is this thing p = what is this equal to?

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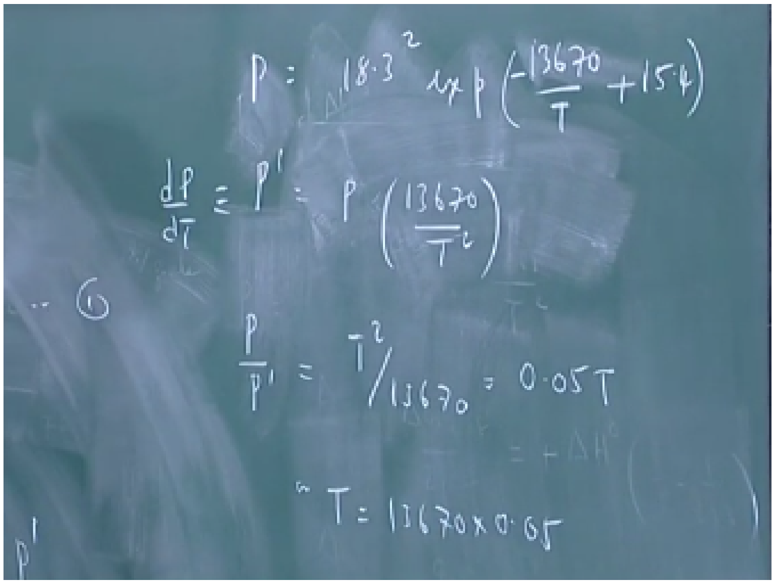

$$P = 18.3^2 \exp\left(\frac{-13670}{T} + 15.4\right)$$

$$\frac{dP}{dT} \equiv P' = P\left(\frac{13670}{T^2}\right)$$

$$\frac{P}{P'} = T^2/13670 = 0.05T$$

$$\therefore T = 13670 \times 0.05$$

I have to 0.2 okay, so you have essentially p = 18.3^2/ exponential of -15.4 + 6835/t so p' I easier to keep the exponential at the numerator I keep to numerator the exponential p = -6835/ t x 2 your right so 13670 / t + 15.4, so p' is going to me back this p and you will get exponential of -13670 no, no I have to just differentiate this that is included in p, if I differentiate this with respect to t I get in to 13670 /t2 p' is dp/ dt.

So p/ p' is t2 /13670 you saying this should be equal to 0.05t or t = 13670 x 0.05 advantage of not simplifying anything as for as possible otherwise you have to computed all these exponential and gone down to details. Otherwise this is come to 683.5 yeah incidentally in all this imperial correlations they are give you cost they will say this is valid only within a range in this case it is just 300 to 800^0 so it is comes within that.

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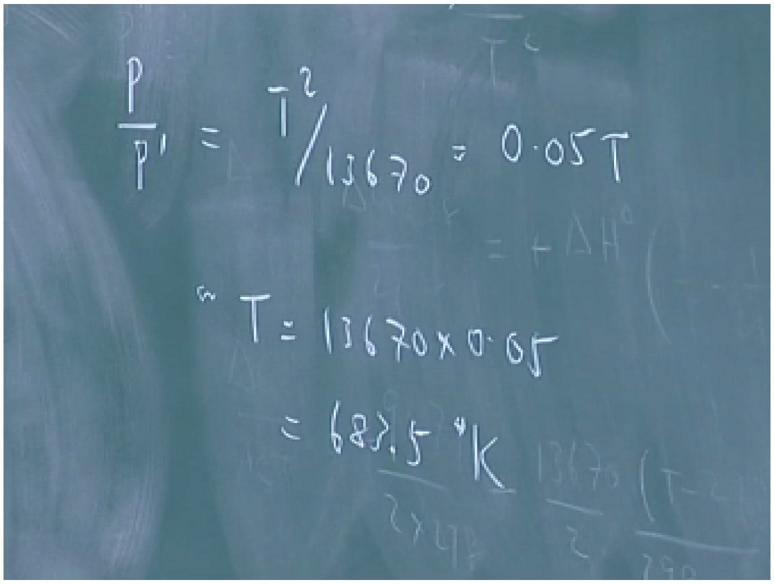

$$\frac{p}{p'} = T^2/13670 = 0.05T$$

$$\therefore T = 13670 \times 0.05$$

$$= 683.5\ °K$$

You have to verify otherwise these since go either because in cost you never know suddenly there will be a step change in case temperature of to which mile shield is allowed a heat exchangers and they will say it is not trying in off, so change to copper or change to something else and their cost different will be huge so in all empirical cost correlations you have to be very careful simply depends on the local market prices, so what is the pressure come out to be 3. 36, actually the cost correlation was actually much more complication then this I think it is given in old issue of industrial engineering chemistry 1947 or 48 I do know if there is a tissues even available here.

Because it is to illustrate the principal I simplified it to this form it is actually given as a long polynomial in pressure and so on some but the principle is prevail simply and eventually your provably solve it on the computer anyway, so this is typical it is just compression calculations but otherwise the principle of it is fairly straightforward because it is three your k φ calculate you have to verify one more step once you know p you can calculate your kφ and check that it is in fact to approximately one.

Any case you do not tell an industry top rate at 3.36 atmosphere you probably give them 3 and half some rounded of number at the fellow is the pressure gave that fluctuates widely, so you want know where these actually reading 3.5 or you know probably within point + or – 0.5, I will take another example this is simultaneous reaction I have got some more data. So every time what happens is you have the equilibrium equations plus special constrains could be in the form of a volume of a reactor it could be in the form of total volume being constant could be in the form of before I take simultaneous reactions let me give you another example this is h-f.

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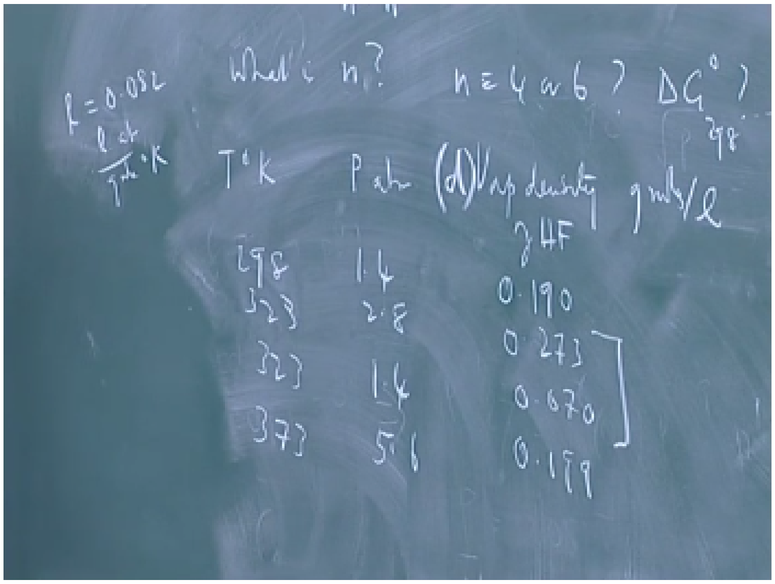

R = 0.082 l atm / gmole °K

What is n?

n = 4 or 6 ? ΔG°_{298} ?

T°K	P atm	(d) Vap density of HF gmoles/l
298	1.4	0.190
323	2.8	0.273
323	1.6	0.070
373	5.6	0.199

H-f is known to polymerize in the gas phase it does not exist as HF this is such a Hn Fn the question is what is M? Usually there is some guests about it n = 4 or 6 were asking you to find out from experimental data on the reaction whether n is four or six the data given under the following form a temperature in degrees came your pressure is given in atmospheres and then the vapor density is given in gram moles per liter if it says vapor density of HF it means the density has been measured assuming that the gas is HF it may actually be h4 f 4 h6 f 6 etcetera.

So the data given as 393 I am sorry 298 the other where 298 and then two measurements at 323 the pressure is given this is two different pressures and then 373 also and 5.6 the vapor density 0.190, 0.273, 0.070, and 0.199, what you are asked to do is first what is N? And then find Δ G0 and Δ H 0 this is given at different temperatures these are asked at 298.

Another silly thing but you have to be careful in reaction equilibrium because you are taking these Exponentials so in you end up with the order of magnitude errors and because you have no industrial exposure as such you do not have a feel for numbers you do not know whether conversion is supposed to be 0.1 or 0.9 we will end up so you have to be careful numbers as far as possible do not do that calculation till the end, then if you are fortunate you do not have to do the calculation at all you didn't have to do an exponential calculation except for constant how will you proceed with this, how will you find out, how will you test the hypothesis? Start off is always initial you have say n moles and 0 modes at equilibrium you need to using HF let us assume there are X moles here then this is n x 1 – X, so total moles is n - n – 1 x x.

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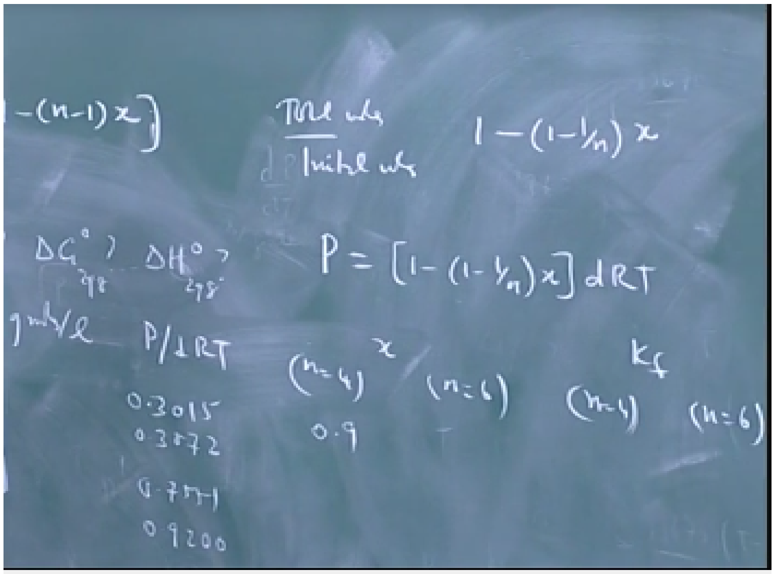

So compared to the initial moles total moles by initial moles and the factor of one – I am just dividing by if you had measured the density as HF this is what you would have got but the actual number of moles is 1 – 1- 1 / n x X depending on the fraction converted to right. So the density if you want to you have P the pressures are quite small we will assume ideal gas you will get essentially number of moles which is 1 - 1 -1 - n x X x D RT this is D, the vapor density is D.

Assuming ideal gas they give you an equation of state you can use the equation of state if it had remained shf then you can verify that P by D RT if you put n = 1for example, then that term will disappear you can verify if p = d RT you can see it is not, how you proceed further what your care for the reaction? KF is kφ x P / total number of moles to the power Δ μ x K n will take K fee as one pressure is Kostas known total number of moles n - 1 X^ the change in number of moles is 1- n this is n moles giving you 1mole, so it is 1 - n then you have K and K n is simply X / n x1 - X^{n}.

Now I have got two readings at 323 the same temperature put a different pressure KF has to be the same for those two, so we will do the KF calculation here for n = 4 and KF for n = 6 this 4 and 6 are guests on the basis of the structure of HF the way the valence bonds are stuck and so

on. So you have no bit of chemistry and some feet in this case there you are told that say either 4 or 6 that they do not know or else you can try out N = 1, 2, 3, 4, 5, 6, so in this case you get two possibilities KF for n = 4 is simply 1 / P ^{3} this is 4 - 3x^{3} x x / 4 x 1- x $^{4.}$
So you have P / D RT that you can calculate here I strike this off before you do this you have to this P / D RT D is given P is given CC atmosphere so make sure our is in the right units you calculate your PV D RT from P by D RT you can get n in terms of you get you can get n index you get n in terms of X or X in terms of N and X for N = 4 and n = 6 then you do the KF calculation here from here X = P / D RT it is 1 - P / D RT/ 1 - 1 / 1/ n.

Once you have care then you can calculate KF for N = four and N = 6, so can you run those through this at the calculator what is P / D RT here are T you have to take the temperature given I think it says 300^{0} temperature is here sorry, so R of course you can take our as 82 cc atmospheres per gram so you have to do this 1.4 / D into this into this if this is litter sorry , this is 0.08 two litters you are take it in litters. So do it in little atmospheres, so tell me what P by D RTS in these four cases yeah this 1.30 yes 38 okay, next 9200 okay then X for X is simply 1- X for M = 4 1 - P / D RT.
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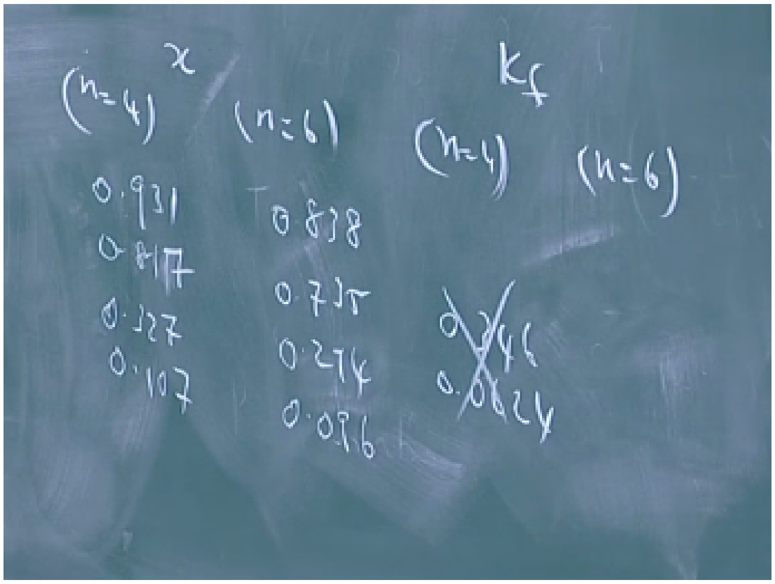

This is 1 / 4, so is 3 / 4 x 4 / 3and X 4 N =6, 6 / 5 x 1 - D / D are bond point name do the numbers carefully first one is a 27 is this is 9 3 1 okay, second point this is all for N = 4 for N = 6 it is actually nearly 80% of this you can just calculate 0.8 times because you are doing the same one - so if you do 0.8times much since your original calculations are good to three decimal places I would not take more this is for but this is 0.8 times this rate because it is six by five by four by three into this is how much you should get 0.8times this because this is simply 6/5 this divided by this is simply 0.8 right this by this because you get 6/5/4/3 2 and 3.

Oh! 9.9 x sorry your right okay till 0.838 09 okay now for finally for the truth kf this is the test in fact you need to do these two first because if K F is not constant at a given temperature then that model is not right, so you need to do the middle ones the expressions are different remember for K F for M = for n = 6 this is 6 - 5 X^5 x X / 6 x 1 – $X^{6 =}$ 4 what is the value? 0.34 okay, not six to four so this sort of rules it out but what about N =6.

Since it is your last option it will be right not 698 not 698 and 0698 is saved, so once you have got that you take an average value for this then you calculate this and you calculate this value then you calculate your Δ g0 and your ΔH zero by differentiation that means you should really plot in this cases you got a lot of scatter.

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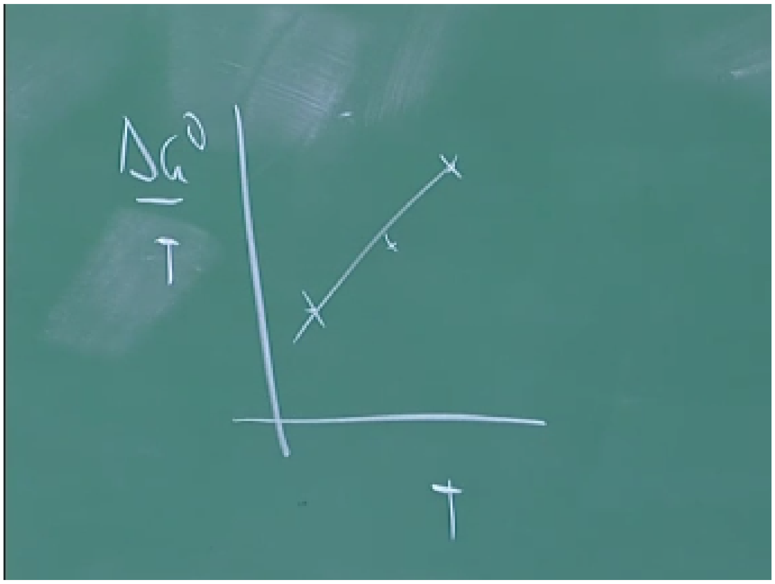

So you have got to plot ΔG 0 / 298 I am sorry by T it is D /DT of this against T D / DT is ΔH zero so we will get a straight line so we will get to cut only three points so you draw a straight line and take the slope of that it should give you $\Delta H /T^2$ you are actually asked to calculate it only at 298 if you do this once you get some idea of the kinds of errors you can expect because this way put this particular vapor density measurement is a very accurate measurement it was taken directly from Journal of chemical engineering data.

And it has the this is about as accurate as you can get to 300 density measurements this itself is pretty unambiguous you have got only one percent error essentially, but in many cases you have to make a judgment when you have to decide that this is good enough or within 5 % this is alright so the actual crucial part here was this relating the vapor density but it is always given in terms of the description of the molecule if it says HF then means vapor density is reported assuming that all molecules are richer.

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