Lecture – 49
Effect of Temperature on the Equilibrium Constants

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Welcome!

Let us begin today by considering the effect of temperature on the equilibrium constant. We have seen equilibrium constants for reactions and their relationship to the standard chemical potential in the previous class. This class, we will start looking at the effect of temperature on the equilibrium constant. Let us first recognize that mu i naught, the standard chemical potential – this is a part of mu i equals mu i naught plus RT ln f i or equivalent – mu i naught is … a function of only temperature. Therefore, this equation 6.18

$$- RT \ln K_p = \sum_i \nu_i \mu_i^0$$

this is what we had derived in the last class. And, this is also the relationship between the equilibrium constant and the standard chemical potential.

This equation, let us rewrite by recognizing the functionality of T as ln of K p … let us take T to the other side, RT to the other side. Minus 1 by R, there is also minus here, sum over nu i mu i naught by T. … Since mu i naught is a function of T, let us group this T along with mu i naught to enable further manipulations with much ease.

$$\ln K_P = -\frac{1}{R} \sum v_i \left(\frac{\mu_i^0}{T}\right)$$

Let us call this equation 6.29. This is why we did it – we are going to differentiate this expression; … when we differentiate, it is good to know the functionalities clearly, and that is why we had grouped it with mu i naught. mu i naught by T is inside the sum here. The product is nu i mu i naught by T.

If, we differentiate equation 6.29 with respect to T … in fact, that is what we are looking for; we are looking for the effect of temperature on the equilibrium constant. The equilibrium constant that we have considered first is K p. So, we get d ln K p dT is nothing but minus 1 by R sum over nu i; nu i is just a stoichiometric co-efficient, not a function of temperature. Therefore, the function of temperature is mu i naught by T alone. Therefore, this becomes d dT of mu i naught by T.

$$\frac{d \ln K_P}{dT} = -\frac{1}{R} \sum v_i \frac{d\left(\frac{\mu_i^0}{T}\right)}{dT}$$

Let us call this equation 6.30.

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We know from Eq. 4.1 that

$$\mu_i = \mu_i^0 + RT \ln P\, y_i$$

Dividing the above equation throughout by T, we get

$$\frac{\mu_i}{T} = \frac{\mu_i^0}{T} + R \ln P + R \ln y_i \qquad \text{Eq. 6.31}$$

At constant pressure, and constant composition, we get

$$\left(\frac{\partial \left(\mu_i / T\right)}{\partial T}\right)_{P,ni} = \left(\frac{d \left(\mu_i^0 / T\right)}{dT}\right) \qquad \text{Eq. 6.32}$$

We know from equation 4.1 … 4.1 is just the definition of the chemical potential

$$\mu_i = \mu_i^0 + R T \ln P y_i$$

We are still with the perfect mixtures. So, mu i equals mu i naught plus RT ln P y i. Let us divide this equation throughout by T. Then we get

$$\frac{\mu_i}{T} = \frac{\mu_i^0}{T} + R \ln P + R \ln y_i$$

I have just split this term. This is ln of a in to b that is ln of a plus ln of b; and there is an RT that is multiplying. So, you have RT ln P plus RT ln y i. RT ln P by T gives you R ln P plus, similarly, R ln y i. This is equation 6.31.

Now, if we assume conditions of constant pressure and constant composition – quite easy to see that pressure remains a constant, and the composition as represented by the mole fraction that remains a constant. And therefore, the derivative with respect to T of mu i by T, dou dou T of mu i by T at constant pressure and constant composition, here indicated by n i but here indicated by y i, the constancy just means the same but let me explicitly write n i here.

So, dou dou T mu i by T at constant P n i … on the right hand side becomes d by dT mu i naught by T gives that is a function of only the temperature. I have taken the total derivative here and these two are constants. Therefore, they are not functions of temperature. Therefore, their derivatives go to zero. They are constant values as far as temperature variation goes and therefore, they can be taken as a zero.

$$\left(\frac{\partial \left(\mu_i / T \right)}{\partial T} \right)_{P, ni} = \left(\frac{d \left(\mu_i^0 / T \right)}{dT} \right)$$

Let us call this equation 6.32.

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Using equation 5 15 – you remember? This is the third equation that we derived when we took a detour in the module 5. Now, it is coming in handy.

$$\left(\frac{\partial \left(\mu_i / T \right)}{\partial T} \right)_{P, \, n_i} = -\frac{\bar{H}_i^T}{T^2}$$

So, on one hand, from equation 5 15 we have dou mu i by T dou T at constant P n i equals minus H i T hash by T squared; and as a part of this equation, we have dou mu i by T dou T at constant P n i equals d dT of mu i naught by T. Therefore, we can since the left hand sides are equal we can equate the right hand sides. Therefore, 6.32 can be written as

$$-\frac{\bar{H}_i^T}{T^2} = \left(\frac{d \left(\mu_i^0 / T \right)}{dT} \right)$$

Let us call this equation 6.33. The right hand side is a total derivative since mu i naught is a function of temperature alone. The partial derivative that we had taken earlier becomes a total derivative here.

Now, equation 6.33 says something important. It implies that the partial molar entropy, H i T hash, is a function of temperature alone. And, more importantly, it will have the same value for

all values of the composition, because it is independent of the composition. Rather it is a function of temperature alone; it is going to be independent of pressure or composition. Therefore, this will have the same value for all values of the mole fraction, even if the mole fraction equals 1. In other words, even if it is a pure component this equation must be valid ... that is a powerful statement here.

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For the pure component i the partial molar value can be replaced by the molar value

Thus, Eq. 6.33 can be written as

$$-\frac{H_i}{T^2} = \left(\frac{d\left(\mu_i^0/T\right)}{dT}\right) \qquad \text{Eq. 6.34}$$

Therefore, Eq. 6.30 can be written as

$$\frac{d\ln K_P}{dT} = \frac{1}{RT^2}\sum v_i H_i \qquad \text{Eq. 6.35}$$

Therefore, for the pure component i the partial molar value can be replaced by the molar value. This equation is anyway going to be valid ... here, this equation 6.33 is anyway going to be valid, because of the function of temperature alone. And therefore, equation 6.33 can be written as minus H i by T squared – instead of the partial molar value, I have taken the molar enthalpy here – minus H i by T squared equals d dT of mu i naught by T.

$$-\frac{H_i}{T^2} = \left(\frac{d\left(\mu_i^0/T\right)}{dT}\right)$$

So, remember our aim was to get the variation of equilibrium constant with temperature. We are in the process ... should never lose track of whatever we are trying to do, when we are in the middle of algebra. That way it helps us keep our sanity.

Equation 6 34 is this, and therefore, equation 6.30 can be written as … equation 6.30 was nothing but the relationship … you know we had differentiated ln of K p equals minus 1 by R … so on and so forth … this will come to you right away. If not, you can go back and look at equation 6.30. d ln K p by T equals 1 by R T squared sum over nu i H i.

Let, me just tell you how this comes about by going back a little bit. Equation 6.30 was this. d ln K P d T equals minus 1 by R sum over nu i d dT of mu i naught by T. Now, we have a relationship for d dT of mu i naught by T in terms of the molar enthalpy itself. That was minus H i by T. Therefore, if you take T out here you will get plus you know there is a minus one by T here. Therefore, if you take T out here, you get plus one by RT here, and this would be nu i H i summed over all i. And, that is what we have said here … coming up in a minute … d ln K p dT equals one by R T squared sum over all i nu i H i. So, this is a useful expression this gives the variation of the equilibrium constant K p with respect to temperature in terms of the enthalpies of the components involved in the reaction.

This is something that you are used to doing right from higher secondary school. You know … sum over nu i H i is how you found your delta H for the various reactions, if you recall that process. … You took the enthalpies of the products summed them up; enthalpies of the reactants, summed them up; subtracted enthalpy of the reactants from the enthalpy of the products. That formally written in a compact notation is this … sum over nu i H i.

$$\frac{d \ln K_P}{dT} = \frac{1}{RT^2} \sum \nu_i H_i$$

Let us call this equation 6.35.

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$$\sum \nu_i M_i = 0$$

for a reaction written like this as just mentioned. Sum over nu i H i … recall that nu i is positive for products on the right hand side of the chemical expression, bio-chemical expression. nu i is negative for the reactants on the left hand side of the chemical expression. This nu i H i summed over all i is nothing but the enthalpy change … of the reaction.

$$\sum \nu_i H_i = \Delta H$$

This is equation 6.39.

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Thus

$$\frac{d \ln K_P}{dT} = \frac{\Delta H}{R T^2} \qquad \text{Eq. 6.40}$$

Eq. 6.40 is known as the Van't Hoff's equation

Starting with Eq. 6.27

$$- RT \ln K_f = \sum_i \nu_i \mu_i^0 \qquad \text{Eq. 6.27}$$

a similar exercise as above yields:

$$\frac{d \ln K_f}{dT} = \frac{\Delta H}{R T^2} \qquad \text{Eq. 6.41}$$

Therefore,

$$\frac{d \ln K_P}{dT} = \frac{\Delta H}{R T^2}$$

So, this gives us an easy method of measuring the variation or estimating the variation of the equilibrium constant with temperature. Just integrate this expression; then we have the kind of relationship that we are looking for, or the estimate that we are looking for. This is equation 6.40. And, this equation, d ln K p dT equals delta H by R T squared … has a special name. It is called the Vant Hoff equation. Now, that you have seen this, we have worked out a means by which we get the … dependence on temperature of K p in terms of the enthalpy of the reaction, and of course, the temperature of the system and so on, what I would like you to do is: starting with equation 6.27 – I will show you what equation 6.27 is – I would like you to derive the same expression or the same dependence for a slightly different equilibrium constant.

As we have seen earlier, there are various equilibrium constants. You know this also from the higher secondary school time onwards. We have K p, we have K c, we have K y, we have K f, and what we are interested in here is K f.

$$- RT \ln K_f = \sum_i \nu_i \mu_i^0$$

This is equation 6.27. Start with this please, minus R T ln K f equals sum over nu i mu i naught. Since this derivation which lasted about five or six slides here with a lot of thought, I am going to give pretty much a lot of time for you … may be about twenty, twenty five minutes. Take that and derive the dependence; the temperature dependence of K f the same way that we derived the temperature dependence of K p.

Go ahead please, take about twenty to twenty five minutes and derive this. I am asking you to derive this here, because there are some slight variations and when you are faced with the variations … that is when you start thinking, and that is when you start understanding the various relationships a little better. The overall scheme is the same but the details are a little different. So, please go ahead and derive this; go ahead, please.

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The relationship that we are looking for … you can check whether you got the same … is

$$\frac{d \ln K_f}{dT} = \frac{\Delta H}{R T^2}$$

Just check whether you got that. Let us call this equation 6.41.

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Over a small range of temperature, ΔH can be assumed to be independent of temperature, and hence, Eq. 6.40 can be written as

$$\ln\frac{K_{P2}}{K_{P1}} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Eq. 6.42

If the temperature range is small, small enough so that the enthalpy change of the reaction can be assumed to be independent of temperature. In other words the delta H is considered a constant in the range of temperatures that we are talking about. It is not exactly a constant, but its variation is small enough that the variation can be neglected. Then, this equation 6.40 can be written as – you know when we integrate that, we are trying to find out a value of K p 2 given a value of K p 1. So,

$$\ln\frac{K_{P2}}{K_{P1}} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

This is equation 6.42 … this comes from the integration of equation 6.40. Let us go back to equation 6.40 to see how that comes about. This is equation 6.40 for K p.

You can do the same thing for 6.41, K f. If we integrate this, so integral from T 1 to T 2 … in this case it will be d ln K p integrated from K p 1 to K p 2. And here, it will be integral from T 1 to T 2, delta H by R T squared dT. If we do that, then this T power minus two and therefore, it becomes minus T power minus one and so on … the integral … Therefore, you will get ln of K p 2 by K p 1 equals delta H by R, 1 by T 1 minus 1 by T 2. The negative sign comes about because of the negative that arises as a result of the integration. We will call this equation 6.42, and this is actually the useful expression for finding out the temperature dependence of the equilibrium constant. In other words, if one equilibrium constant at a particular temperature is known, then we can find another equilibrium constant at another temperature, T 2.

Let us see … whether we are justified in starting up the next topic. No, I do not think we will have time for that. So, let us stop here for now. When we come back in the next class, we will take things forward.