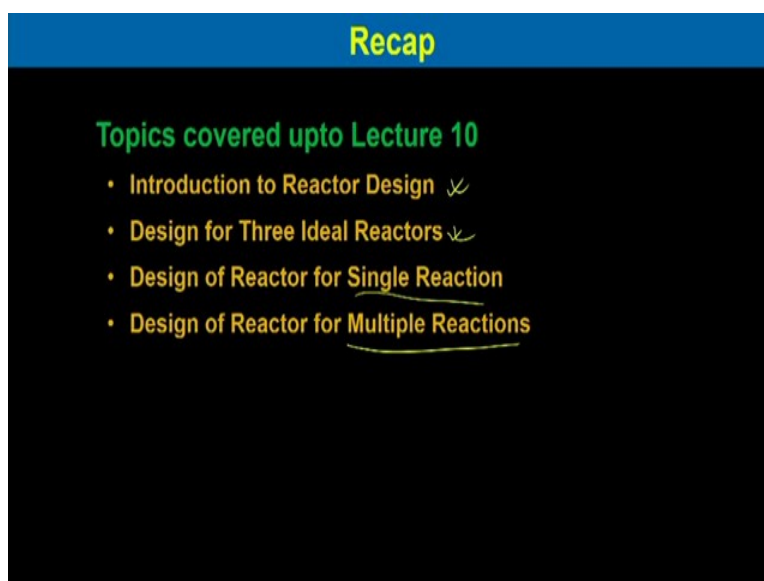


Chemical Reaction Engineering 1
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Lecture 21

Heats of Reaction and Equilibrium Conversion from Thermodynamics

Welcome to the 11th lecture of module 4, in this module we are discussing reactor design before going to this lecture let us have brief recap on the topic or on the reactor design in this module which we have covered so far.

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Up to the last lecture we have covered introduction to the reactor design and there we have considered 3 idealized reactor, ideal batch reactor, ideal plug flow reactor and ideal continuous start and reactor or mixed flow reactor, so this design of 3 ideal reactors we have covered. Then we have considered reactor design for single reaction and when we considered single reaction we have only concerned about the size of the reactor we were not concerned about the product distribution, so that we have covered.

Then we have considered multiple reactions, when we have multiple reactions we mainly concentrated on the product distribution instead of their size requirements, so product distribution is important in case of the multiple reactions and we have considered that for the reactor design of multiple reactions.

In this lecture we will covered mainly the temperature and pressure effects, so the temperature effects and pressure effects so far we have not considered in the reactor design

and we have consider only the isothermal reactor design part. So now we will consider the temperature and pressure effects for the reactors as you know for most of the chemical reactions, either they are exothermic or endothermic in nature, so they are invert with the heat effects, either it cooled down the systems or it will heat up the systems. So, how they effects the reactor design that we will consider in this lecture.

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Module 4: Lecture 11

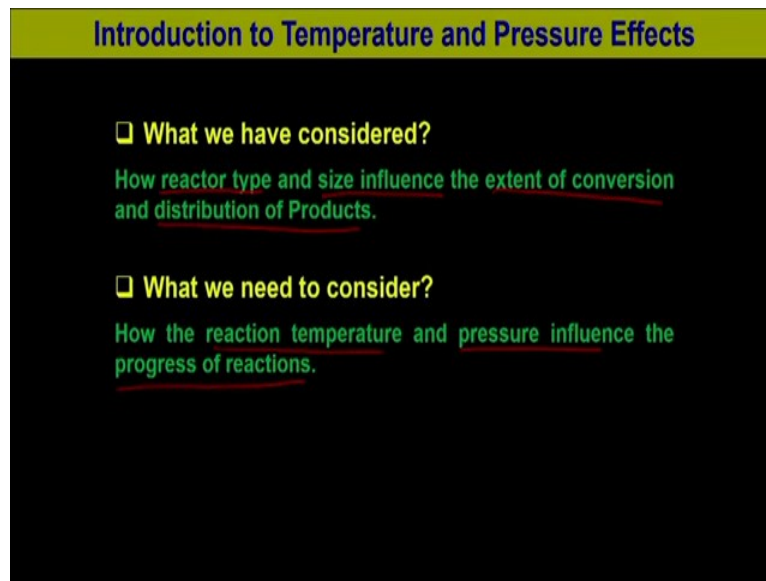
Heats of Reaction and Equilibrium Conversion from Thermodynamics

Lecture Outline

- Introduction to Temperature and Pressure Effects
- Heat of Reactions from Thermodynamics
- Energy Balance
- Equilibrium Constants from Thermodynamics

First, we will consider heat of reactions and equilibrium conversion from thermodynamics, so the brief lecture outline would be introduction to temperature and pressure effects then we will consider heat of reactions from thermodynamics then we will consider energy balance equation and then we will consider equilibrium constant from thermodynamics, while doing so we will mainly calculate the equilibrium conversion.

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Introduction to Temperature and Pressure Effects

- ❑ **What we have considered?**
How reactor type and size influence the extent of conversion and distribution of Products.
- ❑ **What we need to consider?**
How the reaction temperature and pressure influence the progress of reactions.

So far what we have considered, we have considered how reactor type and size influence the extent of conversion and distribution of the products, so this we have considered in the reactor design part in module 4 the type of reactor and the size of the reactor how they influence the extent of reaction and the product distribution and initially we considered single reactions and later we have considered multiple reactions where we were more concerned about the product distribution.

What we need to consider now, we need to see how the reaction temperature and pressure these two influence the progress of the reaction, so influence of temperature and pressure we need to see about the progress of the reaction.

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Introduction to Temperature and Pressure Effects

□ We can follow a three-step procedure

First: Find out how equilibrium composition, rate of reaction, and product distribution are affected by changes in operating temperatures and pressures?

This will allow us to determine the optimum temp. progression.

Second: How heat effects will change the temperature of the reacting mixture?

Then we will be able to propose a number of favorable reactor and heat exchange systems- which closely approach the optimum.

Finally: Economic considerations will select one of these favorable systems as the best.

We can follow a three step procedure, what are them. First find out how equilibrium composition, rate of reaction and product distribution these three affected by change in the operating temperature and pressure.

So initially, we have to find out the equilibrium composition, rate of reaction and product distribution which with change in operating conditions like temperature and pressure, this will allow us to determine the optimum temperature progression, so with increase of temperature how they are changing and then from that we can calculate the optimum temperature how they progress for every steps..

Secondly, we need to see how heat effects will change the temperature of the reacting systems, so when there is a chemical reactions it generally involves heat effects either it absorb heat or it released heat, when it absorb heat we call endothermic reaction when it evolve heat we called exothermic reaction and this change of heat effects how they change the temperature of the reacting mixture that we need to analyze.

This will help us to propose a number of favorable reactors and the heat exchange systems which closely approach the optimum, so based on this heat effects we can see what are the favorable reactors to operate and which heat exchange system weather we need to use heat exchange systems for this purpose that we can propose which will closely resemble to the optimum operating conditions.

And finally economic consideration will select one of these favorable systems as the best, so from the multiple favorable conditions or reactor systems if we propose and finally the economic consideration will choose one of them as the best one.

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Introduction to Temperature and Pressure Effects

Single Reactions

- ❑ **We are concerned**
 - Conversion level
 - Reactor stability

Question of product distribution do not occur

- ❑ **Two important information from thermodynamics**
 - Heat liberated or absorbed for a given extent of reaction
 - Maximum possible conversion

Now, if we have single reaction then for single reactions as we have discussed earlier we are mostly concerned on conversion level it can achieve and the reactor stability whether the reactor is stable up to that operating conditions. But we are not concerned about the product distribution which is not applicable for the single reaction.

Now two important information we can get from thermodynamics, one of them is heat liberated or absorbed for a given extent of reactions, so for a chemical reactions to proceed up to a certain extent of reactions or certain conversion level how much heat it absorb or how much heat it liberates due to the chemical reaction that information we can obtain from the thermodynamics.

The second important information we can get the maximum possible conversion in a given reaction, this is generally happens in case of irreversible reactions that increase of temperature will increase the conversion level, whereas in case of reversible reaction there is some equilibrium conversion at particular conditions, so what would be the maximum possible conversion that we can obtain from the thermodynamics. This maximum achievable conversion is theoretical considerations from the thermodynamics and that is the maximum limit. In real system it is in general it does not achieve to that extents, so that is only from the theoretical consideration in view point of the theoretical considerations.

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Heat of Reaction from Thermodynamics

- ① Nature of the reacting system
- ② Amount of material reacting
- ③ Temperature and pressure of the reacting system.

Heat of reaction = ΔH_r is not known.

$\left. \begin{array}{l} \text{Heat of formation} = \Delta H_f \\ \text{Heat of combustion} = \Delta H_c \end{array} \right\}$ reacting materials.
Temp T_0 or T_1
at 25°C

Now, heat of reactions from thermodynamics, so heat of reactions from thermodynamics the heat which will be absorbed or liberated during a chemical reaction will depend on the three factors, one is nature of the reacting system. Secondly it will depend on how much amount of material it is reacting, so amount of material reacting and the third important thing is that the temperature and pressure of the reacting systems, temperature and pressure of the reacting systems.

So, these are the three factors on which it will depend the amount of heat released or absorbed during a chemical reaction. Now when these three factors can be calculated if we know the heat of reaction, so if we know heat of reaction then we can calculate based on this how much heat it will be absorbed or liberated during a chemical reaction.

If this is not known then we can calculate from the tabulated data on the heat of tabulated data which is on heat of formation that is ΔH_f or heat of combustion that is ΔH_c , these are for the reacting material. And this data are generally tabulated at a certain standard conditions, which is generally at temperature T_0 or T_1 certain standard temperature and at 25 °C usually. So when ΔH_r is not known then these two are calculated from the tabulated data.

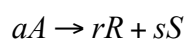
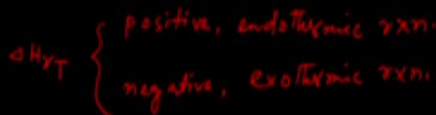
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Heat of Reaction from Thermodynamics

Define Heat of Reaction



□ Heat of reaction is defined at temperature T as the heat transferred to the reacting system from the surroundings when a moles of A disappear to produce r moles of R and s moles of S with the system measured at the same temperature and pressure before and after the reaction.



Now, let us consider the reaction a mole of A is disappearing or dissociating forming r mole of R plus s mole of S, so we can define for this chemical reaction the heat of reaction is defined at temperature T as the heat transferred to the reacting system from the surroundings when a moles A disappear to produce r moles of R and s moles of S with the system measured at same temperature and pressure before and after the chemical reaction.

So, this is say we can write for this reaction, ΔH_r at a temperature T this is generally positive for endothermic reaction and this is negative for exothermic reaction, so positive for endothermic reaction and negative for exothermic reaction, ΔH_{rT} that is heat of reaction at a temperature T, and this it is define so the amount of heat transfer from the surroundings to the reacting systems and when this reactions happens as per there stoichiometric composition and the system would be measured at the same temperature and pressure before and after the chemical reaction.

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Heat of Reaction and Temperature

Energy Balance

$$\left(\begin{array}{l} \text{Heat absorbed} \\ \text{during chem. rxn} \\ \text{at Temp } T_2 \end{array} \right) = \left(\begin{array}{l} \text{heat added to} \\ \text{reactants to change} \\ \text{their temp. from} \\ T_2 \text{ to } T_1 \end{array} \right) + \left(\begin{array}{l} \text{heat absorbed} \\ \text{during rxn} \\ \text{at temp.} \\ T_1 \end{array} \right) + \left(\begin{array}{l} \text{heat added} \\ \text{to products} \\ \text{to bring them} \\ \text{back to } T_2 \\ \text{from } T_1 \end{array} \right)$$

$$\Delta H_{R2} = -(H_2 - H_1)_{\text{reactants}} + \Delta H_{R1} + (H_2 - H_1)_{\text{products}}$$

Subscript 1 refers to temp T_1
 ' 2 ' ' ' ' ' T_2

Now, our first problem is to evaluate the heat of reaction and knowing some values of heat of reactions at temperature T2 we need to calculate a some temperature T1 we need to calculate at temperature T2, so this can be done with the help of energy balance equation. So say(heat absorbed during chemical reaction at temperature T2) = (heat added to reactants to change their temperature from T2 to T1) + (heat absorbed during reaction at temperature T1) + (heat added to products to bring them back to T2 from T1).

So, this is the energy balance equation and in terms of the enthalpies of the reactants and products we can write this as

$$\Delta H_{R2} = -(H_2 - H_1)_{\text{reactants}} + \Delta H_{R1} + (H_2 - H_1)_{\text{products}}$$

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Heat of Reaction and Temperature

Energy Balance

$$\Delta H_{R2} = \Delta H_{R1} + \int_{T_1}^{T_2} \nabla C_p dT$$

Where $\nabla C_p = r \underline{C_{pR}} + s \underline{C_{pS}} - a \underline{C_{pA}}$

$$C_{pA} = \alpha_A + \beta_A T + \gamma_A T^2$$
$$C_{pR} = \alpha_R + \beta_R T + \gamma_R T^2$$
$$C_{pS} = \alpha_S + \beta_S T + \gamma_S T^2$$

So this energy balance expression we can write in terms of the specific heat ΔH_{R2} we can

write as $\Delta H_{R2} = \Delta H_{R1} + \int_{T_1}^{T_2} \nabla C_p dT$ where $\nabla C_p = r C_{pR} + s C_{pS} - a C_{pA}$

So these are the molar specific heat, these are molar specific heat and this are basically function of temperature, so we can write $C_{pA} = \alpha_A + \beta_A T + \gamma_A T^2$ so is a function of temperature similarly other can be written as a function of temperature

$$C_{pR} = \alpha_R + \beta_R T + \gamma_R T^2 \text{ and } C_{pS} = \alpha_S + \beta_S T + \gamma_S T^2$$

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Heat of Reaction and Temperature

Energy Balance

$$\Delta H_{r_2} = \Delta H_{r_1} + \int_{T_1}^{T_2} (\nabla\alpha + \nabla\beta T + \nabla\gamma T^2) dT$$

Heat of rxn. at any T_2 temp.

$$= \Delta H_{r_1} + \nabla\alpha(T_2 - T_1) + \frac{\nabla\beta}{2}(T_2^2 - T_1^2) + \frac{\nabla\gamma}{3}(T_2^3 - T_1^3)$$

At any one temp.

Specific heat of reactants & products.

$$\nabla\alpha = r\alpha_R + s\alpha_S - a\alpha_A$$

$$\nabla\beta = r\beta_R + s\beta_S - a\beta_A$$

$$\nabla\gamma = r\gamma_R + s\gamma_S - a\gamma_A$$

Now, if we substitute this C_{pR} and C_{pS} into this ∇C_p , we would obtain this energy balance

relations would be $\Delta H_{R2} = \Delta H_{R1} + \int_{T_1}^{T_2} (\nabla\alpha + \nabla\beta T + \nabla\gamma T^2) dT$ and which would be this

$$\nabla\alpha = r\alpha_R + s\alpha_S - a\alpha_A$$

Similarly, $\nabla\beta = r\beta_R + s\beta_S - a\beta_A$ and $\nabla\gamma = r\gamma_R + s\gamma_S - a\gamma_A$, so this can be integrated and we can obtain $\Delta H_{R2} = \Delta H_{R1} + \nabla\alpha(T_2 - T_1) + \nabla\beta / 2(T_2^2 - T_1^2) + \nabla\gamma / 3(T_2^3 - T_1^3)$. So knowing the heat of reactions at any one temperature and the specific heat of reactants and products, we would be able to calculate the heat of reaction at any other temperature, so this is the relations between heat of reaction temperature and specific heat.

So, equilibrium constant from thermodynamics, the second law of thermodynamics allows us to calculate the equilibrium constants and hence the equilibrium composition and the equilibrium composition of the reacting systems, but this real system as we have discussed earlier the equilibrium conversion which we obtain from the thermodynamics is basically attainable value which is suggested by thermodynamics, generally does not achievable in the real systems.

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Equilibrium Constants from Thermodynamics

Standard free energy = ΔG°

$$aA \rightarrow rR + sS$$

At temp T:

$$\Delta G^\circ = rG_R^\circ + sG_S^\circ - aG_A^\circ = -RT \ln K = -RT \ln \frac{\left(\frac{f}{f^\circ}\right)_R^r \left(\frac{f}{f^\circ}\right)_S^s}{\left(\frac{f}{f^\circ}\right)_A^a}$$

$f \Rightarrow$ fugacity of component at eqm condition.
 $f^\circ \Rightarrow$ " " " " any arbitrarily selected standard state at temp T.
 $G^\circ \Rightarrow$ standard free energy of a reacting component.
 $K \Rightarrow$ Thermodynamic eqm const.

So, if we consider the standard free energy ΔG , ΔG° and if we consider the reaction $aA \rightarrow rR + sS$ this reaction we can define at temperature T ,

$$\Delta G^\circ = r\Delta G_R^\circ + s\Delta G_S^\circ - a\Delta G_A^\circ = -RT \ln K = -RT \ln \left[\frac{\left(\frac{f}{f^\circ}\right)_R^r \left(\frac{f}{f^\circ}\right)_S^s}{\left(\frac{f}{f^\circ}\right)_A^a} \right]$$

So, this f is the fugacity of component at equilibrium conditions and f° is the fugacity of component at any arbitrarily selected standard state at temperature T and G° is the standard free energy of a reacting component and K is the thermodynamics equilibrium constant for the reactions, K thermodynamics equilibrium constant.

Now, the standard state can be define at a given temperature for gases pure component at atmospheric pressure and if it is solid pure solid at its unit pressure and liquid pure liquid should at its vapour pressure and if it is solute in liquid then 1 molar solution is considered as the standard state. So these are available in the text books the standard conditions we can consider.

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Equilibrium Constants from Thermodynamics

$$K_f = \frac{f_R^r f_S^s}{f_A^a} ; K_p = \frac{P_R^r P_S^s}{P_A^a} ; K_y = \frac{y_R^r y_S^s}{y_A^a}$$

$$K_c = \frac{C_R^r C_S^s}{C_A^a}$$

$$\Delta n = r + s - a$$

$$f^\circ = P^\circ = 1 \text{ atm.}$$

$$K = e^{-\Delta G^\circ / RT} = K_p \underbrace{\left\{ P^\circ = 1 \text{ atm} \right\}^{-\Delta n}}_{\text{unity}}$$

Now, for convenience we can define K_f in terms of the fugacity the equilibrium constants we

can define $K_f = \frac{f_R^r f_S^s}{f_A^a}$. we can write in terms of pressure so $K_p = \frac{P_R^r P_S^s}{P_A^a}$

We can also write in terms of the mole fraction that is $K_y = \frac{y_R^r y_S^s}{y_A^a}$, we can write in terms of

concentration as well that is $K_c = \frac{C_R^r C_S^s}{C_A^a}$ and $\Delta n = r + s - a$, so this is the change of mole between the products and the reactants.

Now, for gaseous system we can consider the standard state is 1 atmosphere and since that pressure is low which is atmospheric pressure generally the fugacity and the pressure are same, so at gas phase reactions at 1 atmospheric pressure we can write $f^\circ = P^\circ = 1$ and so

$K = e^{-\frac{\Delta G^\circ}{RT}} = K_p \left\{ P^\circ = 1 \text{ atm} \right\}^{-\Delta n}$. So this term is always unity but it was kept with the equation to make it dimensionally correct.

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Equilibrium Constants from Thermodynamics

For Ideal Gas

$$f_i = p_i = y_i \pi = C_i RT$$

So, $K_f = K_p$

$$K = \frac{K_p}{(p^\circ = 1 \text{ atm})^{\Delta n}} = \frac{K_y \pi^{\Delta n}}{(p^\circ = 1 \text{ atm})^{\Delta n}} = \frac{K_c (RT)^{\Delta n}}{(p^\circ = 1 \text{ atm})^{\Delta n}}$$

For Solid $\left(\frac{f}{f^\circ}\right) = 1$

So, now if we considered ideal gas, we can write $f_i = p_i = y_i \pi = C_i RT$, so we can write

$$K_f = K_p \text{ and } K = \frac{K_p}{\{P^0 = 1 \text{ atm}\}^{-\Delta n}} = \frac{K_y \pi^{\Delta n}}{\{P^0 = 1 \text{ atm}\}^{-\Delta n}} = \frac{K_c (RT)^{\Delta n}}{\{P^0 = 1 \text{ atm}\}^{-\Delta n}} \text{ and if we take solid}$$

components taking part in the reactions for $\left(\frac{f}{f^\circ}\right) = 1$ So that means the fugacity variation

with respect to the pressure in case of the solid is negligible so $\left(\frac{f}{f^\circ}\right) = 1$

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Equilibrium Constants from Thermodynamics

Equilibrium Conversion

$$\frac{d(\ln K)}{dT} = \frac{\Delta H_r}{R T^2} \quad R = \text{Gas const.}$$

Integrating T_2 & T_1

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H_r}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$\Delta H_r = \text{constant in the temp. range.}$

Now, we will see how we can calculate the equilibrium conversion from thermodynamics. The change in equilibrium constant with respect to temperature is defined as

$$\frac{d(\ln K)}{dT} = -\frac{\Delta H_R}{RT^2}, \text{ now if we integrate with a temperature limit } T_2 \text{ and } T_1 \text{ we can calculate}$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H_R}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

So, R is the universal gas constant T is any temperature here and while integrating it is assume that ΔH_R is considered as constant in this temperature range and hence taken out from the integral sign. So this is from where knowing the K1 at a particular temperature we can calculate K2.

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Equilibrium Constants from Thermodynamics

Equilibrium Conversion

$$\ln \frac{K_2}{K_1} = \frac{1}{R} \int_{T_1}^{T_2} \frac{\Delta H_r}{T^2} dT.$$

$$\Delta H_r = \Delta H_{r0} + \int_{T_0}^T \nabla C_p dT.$$

$$R \ln \frac{K_2}{K_1} = \nabla \alpha \ln \frac{T_2}{T_1} + \frac{\nabla \beta}{2} (T_2 - T_1) + \frac{\nabla \gamma}{6} (T_2^2 - T_1^2) + \left(-\Delta H_{r0} + \nabla \alpha T_0 + \frac{\nabla \beta}{2} T_0^2 + \frac{\nabla \gamma}{3} T_0^3 \right) \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Now if there is variation of delta Hr in the temperature range that should be accounted for, so

we can write in that case $\ln\left(\frac{K_2}{K_1}\right) = \frac{1}{R} \int_{T_1}^{T_2} \frac{\Delta H_R}{T^2} dT$, now this $\Delta H_R = \Delta H_{R0} + \int_{T_0}^T \nabla C_P dT$

Now, if we substitute this ΔH_R over here and then putting the values of delta Cp which we have obtained earlier and then we can integrate and the integration will give

$$R \ln\left(\frac{K_2}{K_1}\right) = \nabla \alpha \ln\left(\frac{T_2}{T_1}\right) + \frac{\nabla \beta}{2} (T_2 - T_1) + \frac{\nabla \gamma}{6} (T_2^2 - T_1^2) + (-\Delta H_{R0} + \nabla \alpha T_0 + \frac{\nabla \beta}{2} T_0^2 + \frac{\nabla \gamma}{3} T_0^3) \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

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Example 1

Consider the following elementary reaction:

$$A \leftrightarrow R \quad \Delta G_{298}^0 = -14130 \text{ J/mol} \text{ and } \Delta H_{298}^0 = -75300 \text{ J/mol}$$

$$C_{pA} = C_{pR} = \text{constant}$$

(a) Determine the equilibrium conversion between 0°C and 100°C. Plot temperature versus conversion.

(b) What restriction should be placed for the reactor operating isothermally if we are to obtain a conversion of 75% or higher?

Solution

$$\nabla C_p = 0$$

$$\Delta H_R = \Delta H_{R,298} = -75300 \text{ J/mol}$$

$$K = \exp\left(-\frac{\Delta G_{298}^0}{RT}\right) = \exp\left(\frac{14130 \text{ J/mol}}{(8.314 \text{ J/mol}\cdot\text{K})(298\text{K})}\right) = 300$$

Now, let us take an example, so consider the following elementary reaction say $A \rightarrow R$ this is reversible reaction where $\Delta G_{298}^0 = -14130 \text{ J/mol}$ and $\Delta H_{298}^0 = -75300 \text{ J/mol}$ and $C_{pA} = C_{pR} = \text{constant}$.

Now, we need to determine the equilibrium conversion between 0 degree centigrade and 100 degree centigrade and then plot the temperature versus conversion. Second is for restriction should be placed for the reactor operating isothermally if we are to obtain a conversion of 75 percent or higher.

So, let us solve it, as we can see the specific heat C_{pA} and C_{pR} so these are given constant. So since C_{pR} and C_{pH} constant, $\nabla C_p = 0$ so that means the heat of reaction ΔH_R is independent of the temperature, so in that case we can write $\Delta H_R = \Delta H_{R,298} = -75300 \text{ J/mol}$

Now, we can calculate the equilibrium constant at 25 degree centigrade from the equations

which is known $K = \exp\left(-\frac{\Delta G_{298}^0}{RT}\right) = \exp\left(\frac{14130 \text{ J/mol}}{(8.314 \text{ J/mol}\cdot\text{K})(298\text{K})}\right) = 300$

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Example 1

Consider the following elementary reaction:
 $A \leftrightarrow R$ $\Delta G_{298}^{\circ} = -14130 \text{ J/mol}$ and $\Delta H_{298}^{\circ} = -75300 \text{ J/mol}$
 $C_{pA} = C_{pR} = \text{constant}$

(a) Determine the equilibrium conversion between 0oC and 100oC. Plot temperature versus conversion.
 (b) What restriction should be placed for the reactor operating isothermally if we are to obtain a conversion of 75% or higher?

Solution

$$\ln \frac{K}{K_{298}} = -\frac{\Delta H_r}{R} \left(\frac{1}{T} - \frac{1}{298} \right)$$

$K_{298} = 300$
 $\Delta H_r = -75300 \text{ J/mol}$

$$\Rightarrow K = K_{298} \exp \left[\frac{-\Delta H_r}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right]$$

$$= 300 \exp \left[\frac{75300}{8.314} \left(\frac{1}{T} - \frac{1}{298} \right) \right]$$

$$= 300 \exp \left[\frac{75300}{8.314 T} - 30.393 \right]$$

Now, since the heat of reactions do not change with temperature the equilibrium constant at

any temperature T we can write $\ln(K/K_{298}) = -\frac{\Delta H_R}{R} \left(\frac{1}{T} - \frac{1}{298} \right)$. So if we rearrange this we

can write $K = K_{298} \exp \left[-\frac{\Delta H_R}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right]$.

Now, if we substitute the values K 298 we have calculated which is equal to 300 and

$$K = 300 \exp \left[\frac{75300}{8.314} \left(\frac{1}{T} - \frac{1}{298} \right) \right]$$

$$K = 300 \exp \left[\frac{75300}{8.314 T} - 30.393 \right]$$

So using this expression if we choose a different temperature we can calculate K values.

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Example 1

Consider the following elementary reaction:
 $A \leftrightarrow R$ $\Delta G^\circ_{298} = -14130 \text{ J/mol}$ and $\Delta H^\circ_{298} = -75300 \text{ J/mol}$
 $C_{pA} = C_{pR} = \text{constant}$

(a) Determine the equilibrium conversion between 0oC and 100oC. Plot temperature versus conversion.
 (b) What restriction should be placed for the reactor operating isothermally if we are to obtain a conversion of 75% or higher?

Solution

At eqn: $K = \frac{C_R}{C_A} = \frac{C_{A0} X_{Ae}}{C_{A0}(1-X_{Ae})} = \frac{X_{Ae}}{1-X_{Ae}}$
 $\Rightarrow X_{Ae} = \frac{K}{K+1}$

Now, at equilibrium, $K = \frac{C_R}{C_A} = \frac{C_{A0} X_{Ae}}{C_{A0}(1-X_{Ae})} = \frac{X_{Ae}}{(1-X_{Ae})}$, from here we can write

$X_{Ae} = \frac{K}{K+1}$ now with this two relations we can calculate K first with a particular temperature

and using that K values we can calculate the XAe values.

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Example 1

Consider the following elementary reaction:
 $A \leftrightarrow R$ $\Delta G^\circ_{298} = -14130 \text{ J/mol}$ and $\Delta H^\circ_{298} = -75300 \text{ J/mol}$
 $C_{pA} = C_{pR} = \text{constant}$

(a) Determine the equilibrium conversion between 0oC and 100oC. Plot temperature versus conversion.
 (b) What restriction should be placed for the reactor operating isothermally if we are to obtain a conversion of 75% or higher?

Solution

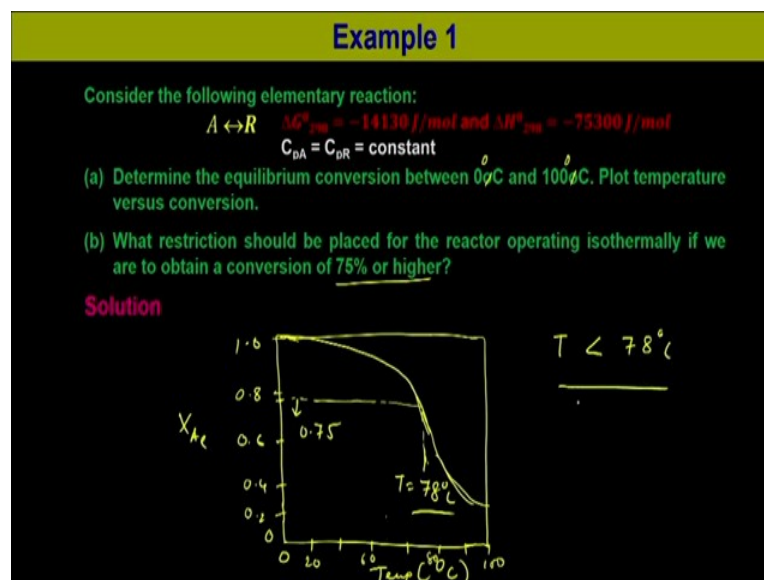
$K = 500 \times \exp\left[\frac{75300}{8.314 \times T} - 30.393\right]$ $X_{Ae} = \frac{K}{K+1}$

oC	Selected Temp	K	X _{Ae}
5	278	2700	0.999+
15	288	860	0.999
35	308	110	0.991
55	328	18	0.949
75	348	3.8	0.791
95	368	0.92	0.48

So, we can obtain the table say at selected temperature K is equal to 300 into 75300 divided by 8.314 into T minus 30.393 this is exponential then we can calculate XAe is equal to K by K plus 1. So at a selected temperature say 5 degree centigrade and which is temperature we can make it say degree centigrade and kelvin, so if it is 5 degree then it is say 278 say 15 288 say 35 3 naught 8 we can 55 say 328 we can do 75 which is 348 and say 95 say 368, so this are the temperature say at a particular interval we can select and we can put into this equation.

So, we can obtain so this is about 200 2700 and this is about 860 then this is about 110 this is about 18.4 or 18 and this is about 3.8 and this is about 0.92, so the corresponding values we can calculate XAe putting this K values over here this would be point close to 1 and this is about 0.999 then this is about 0.991 this is 0.949 this is about 0.791 and this is about 0.48.

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Now, we can plot the conversion versus temperature say if we plot say degree centigrade and in temperature and the conversion we would obtain say this is 00 and this temperature in degree centigrade and say this is 0 and this is 20 say 40 60 80 100 120 140, so 20 is 20 60 80 and 100 conversion is 0 then 0.2, 0.4, say 0.6, 0.8 and 1, so our conversion starts at a very low temperature say 5 degree so it is close to 1 and conversion starts like this and it goes down and like this say upto 0.4.

So, now we can so this is the XAe equilibrium conversion versus temperature plot, now so the first problem is we can determine the equilibrium conversion between this temperature 0 degree centigrade to 100 degree centigrade, so in between and we can plot the you know

temperature versus conversion plot now what restriction should be placed for the reactor operating isothermally if we are to obtain a conversion 75 percent or higher.

Now, at 75 percent say it is very close to over here and we can locate the equilibrium conversion which is close to so if we go from here to here and come down, so this temperature is about equilibrium conversion at the 75 percent, so this is 0.75 percent 75 percent conversion so this temperature T is about 78 degree centigrade. So if we had to achieve this 75 percent conversion or higher we had to be below this temperature that means the T should be less than 78 degree centigrade.

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Conclusions from Thermodynamics

- Thermodynamic equilibrium constant is **unaffected** by
 - Pressure of the system ✓
 - Presence or absence of inert ✓
 - Kinetics of the reaction ✓

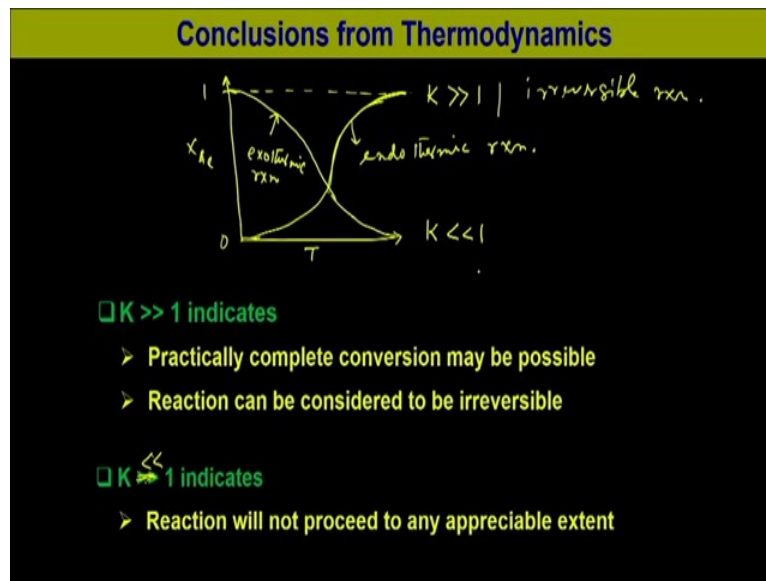
But affected by the temperature of the system

- Equilibrium concentration of materials and equilibrium conversion can be **influenced** by
 - Pressure of the system
 - Presence or absence of inert
 - Kinetics of the reaction

Now, what conclusion we can make from the thermodynamics, we can see that thermodynamic equilibrium constant is unaffected by the pressure of the system, presence or absence of the inert and kinetics of the reaction. So these three parameters pressure of the system inert and the kinetics of the reaction this does not influence or this are unaffected the equilibrium constant.

So, but the equilibrium constant is affected by the temperature of the reacting system so although the equilibrium constants are unaffected by the this parameters but they are equilibrium concentration of the material and the equilibrium conversion does influence by this three parameters pressure of the systems, presence or absence of the inert and kinetics of the reaction. So, these three parameters influence the equilibrium concentration of the materials and the equilibrium conversion.

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Now, if we see the equilibrium conversion versus temperature plot as we have done before we can see that for, so for exothermic reaction we have seen the equilibrium conversion drops with increasing temperature, whereas for endothermic reaction it increases with temperature. So this is for K very very greater than 1 and this is for K very very less than 1, so this is for exothermic this is for endothermic reaction.

So, K very very greater than 1 it indicates that practically complete conversion may be possible and reaction can be considered to be irreversible so this can be considered as irreversible reaction. K very very less than 1, indicates K very very less than 1, indicates the reaction will not proceed to any appreciable extent, so which is the case in case of the so this is for exothermic reaction, so that is very low conversion as we increase the temperature.

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Conclusions from Thermodynamics

- With increase in temperature
 - Equilibrium conversion increases for endothermic reaction
 - Equilibrium conversion decreases for exothermic reaction
- With increase in pressure for gas phase reaction
 - Conversion increases when the number of moles decreases with reaction
 - Conversion decreases when the number of moles increases with reaction
- A decrease in inert for all reactions acts in the way that an increase in pressure acts for gas phase reactions

Now, with increase in temperature the equilibrium conversion increases for endothermic reaction and equilibrium conversion decreases for exothermic reaction. With increase in pressure for gas phase reaction what we can see that conversion increases when the number of moles decreases with reaction and conversion decreases when the number of moles increases with the reaction, this is the case when we increase the pressure for the gas phase reactions.

Whereas, a decrease in inert for all reactions acts in the way that an increase in pressure acts for gas phase reactions, so in this case the effect of inert can be seen for all kind of reactions if we decrease the inert it will act in the same way as with increase in pressure for the gas phase reactions.

So, with this we conclude for the lecture 1 for the calculation of the equilibrium constant and variation of the temperature or calculation of the heat of reactions from the thermodynamics point of view we will continue our discussion for temperature and pressure effects in the next lecture, thank you.