

LECTURE

# 9

# CHE 415

# Chemical Engineering Thermodynamics II

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## **Chemical Reaction Equilibria**



# Learning Objectives for today's lecture

- At the end of this week's lecture, you should be able to:
  - Explain and derive the criteria for chemical reaction equilibrium.
  - Explain the physical significance of chemical reaction equilibrium
  - Conceptualize equilibrium constant: its relationship with the standard free energy and evaluation.
  - Explain the feasibility of chemical reaction from thermodynamic stand point
  - Explain the effect of temperature on equilibrium constant.



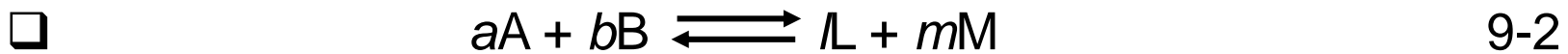
# CRITERIA OF CHEMICAL REACTION EQUILIBRIUM

- At constant T and P, the transfer of materials from one phase to another under equilibrium is found to occur with no change in the free energy.

- Stated mathematically,

$$dG_{T, P}^l = 0 \quad 9-1$$

- This criterion is quite general and not restricted to physical transformations alone.
- Similarly, when a chemical reaction occurs at equilibrium there is no change in the Gibbs free energy of the system, provided the change is taking place at constant T and P.
- Consider a closed system in which a chemical reaction represented by the following general equation has been allowed to reach a state of equilibrium at a given T and P.



- An infinitesimal change is allowed to occur in the system whereby the number of moles of various species change.
- The changes in the number of moles are  $dn_A$ ,  $dn_B$ ,  $dn_L$  and  $dn_M$  for components A, B, L and M respectively.



# CRITERIA OF CHEMICAL REACTION EQUILIBRIUM

- The free energy change for the process occurring at constant T and P is given by

$$dG_{T,P}^t = \sum \mu_i dn_i \quad 9-3$$

- where  $\mu_i$  is the chemical potential of component  $i$ .
- For the reaction under consideration, Eq. 9-3 takes the form

$$dG_{T,P}^t = \mu_L dn_L + \mu_M dn_M + \mu_A dn_A + \mu_B dn_B$$

- By substituting,  $dn_i = v_i d\varepsilon$ , the above equation becomes

$$dG_{T,P}^t = (v_L \mu_L + v_M \mu_M + v_A \mu_A + v_B \mu_B) d\varepsilon \quad 9-4$$

$$= (l \mu_L + m \mu_M - a \mu_A - b \mu_B) d\varepsilon$$

- where  $-a$ ,  $-b$ ,  $l$  and  $m$  are the stoichiometric numbers which are positive for products and negative for the reactants and  $\varepsilon$  is the extent of reaction.
- In general, for an infinitesimal change in a reacting system, we can write Eq.9-4 as

$$dG_{T,P}^t = \sum \mu_i v_i d\varepsilon \quad 9-5$$



# CRITERIA OF CHEMICAL REACTION EQUILIBRIUM

- Since the process is occurring at equilibrium conditions, Eq.9-1 should be satisfied so that

- $$dG_{T,P}^t = \sum \mu_i \nu_i d\varepsilon = 0 \quad 9-6$$

- or

- $$\sum \mu_i \nu_i = 0 \quad 9-7a$$

- This is the criterion of equilibrium for chemical reactions.
- For the present reaction given by 9-2, this criterion means that

- $$(l\mu_L + m\mu_M) - (a\mu_A + b\mu_B) = 0 \quad 9-7b$$

- The left-hand side of Eq. 9-7 is the free energy change  $dG$  accompanying the complete reaction under equilibrium conditions.
- Hence,  $dG = 0$  under equilibrium.



# PHYSICAL SIGNIFICANCE OF CHEMICAL REACTION EQUILIBRIUM

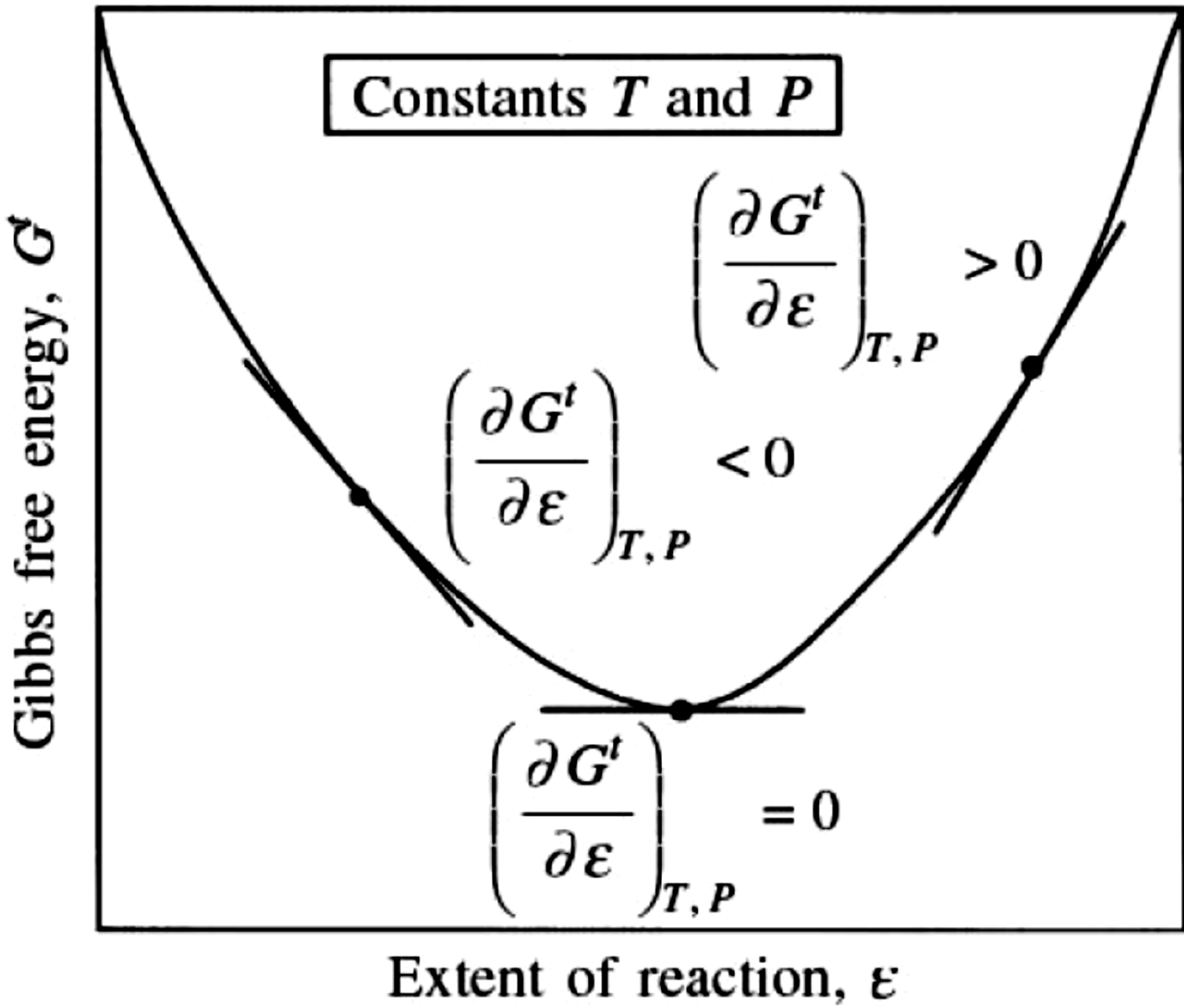
- ❑ Consider a simple chemical reaction equilibrium:  $A \rightleftharpoons B$ .
- ❑ Let the extent of the reaction be  $\varepsilon$ .
- ❑ The change in the number of moles of A =  $-d\varepsilon$  and the change in the number of moles of B =  $d\varepsilon$ .
- ❑ The change in free energy at constant T and P is found out by Eq. 9-5

- ❑ 
$$dG^t = (\mu_B - \mu_A) d\varepsilon \quad 9-8$$

- ❑ This equation can be written in the form.

- ❑ 
$$\left( \frac{\partial G^t}{\partial \varepsilon} \right)_{T,P} = \mu_B - \mu_A \quad 9-9$$

- ❑ Eq.9-9 gives the slope of the curve obtained when the Gibbs free energy is plotted against extent of reaction as in [Fig.9.1](#).
- ❑ The slopes given by Eq.9-9 are not constant because the chemical potentials are functions of composition, which varies as the extent of reaction changes.





# PHYSICAL SIGNIFICANCE OF CHEMICAL REACTION EQUILIBRIUM

- ❑ Since the reaction proceeds in the direction of decreasing Gibbs free energy  $G$ , the forward reaction ( $A \rightleftharpoons B$ ) takes place if  $\mu_A > \mu_B$  and
- ❑ the backward reaction ( $A \leftarrow B$ ) proceeds if  $\mu_A < \mu_B$ .
- ❑ When  $\mu_A = \mu_B$ , the slope of the curve is zero.
  - ❑ This occurs at the minimum of the curve and corresponds to the position of chemical equilibrium.
- ❑ The composition of the reaction mixture at the point where the Gibbs free energy is the minimum is the equilibrium composition at the specified temperature and pressure.
- ❑ The criterion of equilibrium, Eq.9-7, means that **differential displacement of chemical reaction can occur at the equilibrium state**, but without changing the total Gibbs free energy.
- ❑ If the system is not in chemical equilibrium, the reaction occurring must be irreversible and the total Gibbs free energy must decrease at constant  $T$  and  $P$ .





# EQUILIBRIUM CONSTANT

- Considering the chemical reaction given by Eq.9-2



- The equilibrium constant  $K$  or  $K_a$  for this reaction is defined in terms of the activities of the reactants and the products as

- $$K = K_a = \frac{a_L^l a_M^m}{a_A^a a_B^b} = \prod a_i^{v_i} \quad 9-10$$

- where  $a_i$  is the activity of component  $i$  in the reaction mixture and  $v_i$  is the stoichiometric number of  $i$ .
  - Activities of the species appearing in Eq.9-10 are raised to the respective stoichiometric numbers.
- Since the activity is defined as the ratio of the fugacity of the component in the solution to the fugacity in the standard state,

$$a_i = \frac{\bar{f}_i}{f_i^0}$$

- Eq.9-10 can also be written as

- $$K = \prod \left( \frac{\bar{f}_i}{f_i^0} \right)^{v_i} \quad 9-11$$



# EQUILIBRIUM CONSTANT

- For gaseous systems, the standard state chosen is the pure component gas at a pressure at which the fugacity is unity. Therefore,  $f_i^0 = 1$  and Eq.9-11 reduces to:

- $$K = \prod(\bar{f}_i)^{\nu_i} = K_f \quad 9-12$$

- where  $K_f$  is an equilibrium constant in terms of fugacity of the components.

- For liquids and solids, the equilibrium constant  $K$  and  $K_f$  are not numerically equal as standard state fugacities are not unity.

- Another frequently used equilibrium constant in the study of gaseous reactions is  $K_p$ , the equilibrium constant in terms of pressures.

- $$K_p = \prod(\bar{p}_i)^{\nu_i} \quad 9-13$$

- Using the relation that fugacity of a component in a gas mixture is equal to the product of fugacity coefficient and the partial pressure, Eq.9-12 can be written as:

- $$K = K_f = \prod(\bar{\phi}_i \bar{p}_i)^{\nu_i} = \prod(\bar{\phi}_i)^{\nu_i} \prod(\bar{p}_i)^{\nu_i} \quad 9-14$$

- Denoting  $\prod(\bar{\phi}_i)^{\nu_i}$  by  $K_f$ , we can write Eq.9-14 as

- $$K = K_f = K_f K_p \quad 9-15$$



# EQUILIBRIUM CONSTANT AND STANDARD FREE ENERGY

- The criterion of equilibrium, Eq.9-7, can be written for the general chemical reaction represented by Eq.9-2 as

$$\square \quad (l\mu_L + m\mu_M) - (a\mu_A + b\mu_B) = 0 \quad 9-7b$$

- The chemical potential of a component in the equilibrium state of the reaction mixture is related to its fugacity in that state by

$$\square \quad \mu_i = RT \ln \bar{f}_i + C \quad 9-16$$

- Suppose that at the same temperature, but at another state, which may be called the standard state, the free energy of component  $i$  is  $\mu_i^0$ .

Then,

$$\square \quad \mu_i^0 = RT \ln f_i^0 + C \quad 9-17$$

- $C$  is a constant that depends only on temperature.

- Since the temperature in the standard state is the same as that in the equilibrium state,  $C$  can be eliminated from Eq.9-16 using Eq.9-17 as,

$$\square \quad \mu_i = \mu_i^0 + RT \ln \frac{\bar{f}_i}{f_i^0} = \mu_i^0 + RT \ln a_i \quad 9-18$$

- Where  $a_i$  is the activity of species  $i$  in the mixture.

- Expressing the chemical potential of all the components as in Eq.9-18 and substituting in Eq.9-7b, the resulting expression is



# EQUILIBRIUM CONSTANT AND STANDARD FREE ENERGY

$$\square \quad (l\mu_L^0 + m\mu_M^0) - (a\mu_A^0 + b\mu_B^0) + RT \ln \frac{a_L^l a_M^m}{a_A^a a_B^b} = 0 \quad 9-19$$

□ Eq.9-19) can be put into the form:

$$\square \quad (l\mu_L^0 + m\mu_M^0) - (a\mu_A^0 + b\mu_B^0) = -RT \ln \frac{a_L^l a_M^m}{a_A^a a_B^b} \quad 9-20$$

□ That is

$$\Sigma \mu_i^0 \nu_i = -RT \ln \frac{a_L^l a_M^m}{a_A^a a_B^b}$$

□ The left-hand side gives the standard free energy change  $\Delta G^0$ , the free energy change accompanying the reaction when each of the reactants and the products is in its standard state.

□ Using the definition of the equilibrium constant Eq.9-10, the above equation is written as

$$\square \quad \Delta G^0 = -RT \ln K \quad 9-21$$

□ Thus the equilibrium constant is determined by the standard free energy change and the temperature.



# EQUILIBRIUM CONSTANT AND STANDARD FREE ENERGY

- ❑ Therefore, the standard free energy change involved in a chemical reaction depends on
  - ✓ the temperature,
  - ✓ the specification of standard state for each component and
  - ✓ the number of moles involved in the stoichiometric equation under consideration.
- ❑ The numerical values of the equilibrium constant will be of no significance unless accompanied by the specifications for these three factors.



# FEASIBILITY OF A REACTION

- ❑ Following from Eq.9-21, the following guide may be useful as an approximate criterion for ascertaining the feasibility of chemical reactions:
- ❑ When  $\Delta G^0 = 0$ , then  $K = 1$ , the reaction proceeds to a considerable extent before equilibrium is reached.
- ❑ When  $\Delta G^0 < 0$ , then  $K > 1$ , the reaction is favourable, but becomes less favourable as  $\Delta G^0$  increases in the positive direction.
- ❑ When  $0 < \Delta G^0 < 40,000$  kJ/kmol, the reaction may or may not be possible and needs further study.
- ❑ When  $\Delta G^0 > 40,000$  kJ/kmol,  $K < 1$ , the reaction is very unfavourable.
- ❑ It should be noted that many reactions with positive values of  $\Delta G^0$  are certainly feasible from the standpoint of industrial operation. However, such reactions may be carried out at high pressure to overcome the unfavourable free energy change.
- ❑ Hence, there is no well-defined demarcation to separate favourable and unfavourable reactions.
- ❑ For gas-phase reactions, series of hypothetical steps could be used to determine the associated free energy change for the reaction.



# FEASIBILITY OF A REACTION

- ❑ Considering the hypothetical gas-phase reaction:
  - ❑ 
$$aA + Bb \rightleftharpoons lL + mM$$
  - ❑ with the reactants and the products at their standard state.
  - ❑  $\Delta G^0$  accompanying the process in which the reactants at their standard state are converted to products also at their standard state may be calculated via any convenient path.
  - ❑ Let us assume the following computational path for carrying out the reaction, which is represented in [Fig. 9-2](#).
  - ❑ *Step 1:*
    - ✓ The reactants are initially in their pure form and are at their standard state of unit fugacity and at the temperature of the reaction.
    - ✓ Then they are compressed to a fugacity of the reaction mixture at equilibrium.
    - ✓ The free energy change for this process is  $\Delta G_1$ .
  - ❑ *Step 2:*
    - ✓ The pure reactants are introduced to the reaction system through membranes permeable only to single species.
    - ✓ Since the fugacities of the components before and after this step are the same, the free energy change  $\Delta G_2$  for this process is zero, i.e  $\Delta G_2 = 0$ .

*Initial state:*  
pure reactants in their  
standard state with  
fugacities  $f_A^0$  and  $f_B^0$

*Final state:*  
products in their  
standard state with  
fugacities  $f_L^0$  and  $f_M^0$

$\Delta G^0$

$\Delta G_1$

$\Delta G_5$

Pure reactants with  
fugacities  $\bar{f}_A$  and  $\bar{f}_B$

Pure products with  
fugacities  $f_L^0$  and  $f_M^0$

$\Delta G_2$

$\Delta G_4$

Reactants with  
fugacities  $\bar{f}_A$  and  $\bar{f}_B$   
in chemical  
equilibrium

$\Delta G_3$

Products with  
fugacities  $\bar{f}_L$  and  $\bar{f}_M$   
in chemical  
equilibrium







# FEASIBILITY OF A REACTION

## □ Step 3:

- ✓ The introduction of the reactants disturbs the state of equilibrium prevailing in the reaction system.
- ✓ To bring the system back to the equilibrium condition the forward reaction occurs at the given temperature and pressure.
- ✓ According to the criterion of equilibrium, this reaction proceeds without any change in the free energy of the system. Hence,  $\Delta G_3 = 0$ .

## □ Step 4:

- The product gases are separated by means of membranes into pure components at the reaction temperature and pressure.
- As in step 2, the free energy change in this process is zero, i.e  $\Delta G_4 = 0$ .

## □ Step 5:

- The pure components with fugacities equal to  $f_i = \bar{f}_i$  are expanded to standard state fugacities  $f_i^0$ .
- The free energy change for this step,

$$\Delta G_5 = RT \left( l \ln \frac{f_L^0}{\bar{f}_L} + m \ln \frac{f_M^0}{\bar{f}_M} \right) = RT \left( l \ln \frac{1}{a_L} + m \ln \frac{1}{a_M} \right) = RT \ln \left( \frac{1}{a_L^l a_M^m} \right)$$

# FEASIBILITY OF A REACTION

□ As the free energy is a state property, the standard free energy change,  $\Delta G^0$ , for the reaction is equal to the sum of the free energy changes in the five steps.

□ Thus,

$$\Delta G^0 = \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 + \Delta G_5 = RT \ln (a_A^a a_B^b) + RT \ln \left( \frac{1}{a_L^l a_M^m} \right)$$

□ This can be written as

$$\Delta G^0 = -RT \ln \frac{a_L^l a_M^m}{a_A^a a_B^b} = -RT \ln K$$

□ Which is the same as Eq.9-21.



# EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

- ❑ The effect of the operating variables on equilibrium can be qualitatively explained by the *Le Chatelier's principle*, which states that
  - ❑ ***a system at equilibrium when subjected to a disturbance, responds in a way that tends to minimise the effect of that disturbance.***
- ❑ An increase in temperature will shift the equilibrium state in the direction of absorption of heat, i.e. the equilibrium will shift in the endothermic direction if the temperature is raised, for then, energy is absorbed as heat.
- ❑ In a similar way, the equilibrium can be expected to shift in the exothermic direction if the temperature is lowered, for then the reduction in temperature is opposed.
- ❑ Thus, an endothermic reaction is favoured by an increase in temperature and an exothermic reaction is favoured by a decrease in temperature.
- ❑ Or stated in another way, increased temperature favours the reactants in exothermic reactions and the products in endothermic reactions.



# EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

- ❑ The effect of temperature on equilibrium constant is quantitatively expressed by *van't Hoff equation*.
- ❑ The relationship of equilibrium constant to the standard free energy of reaction is given by Eq.9-21.
- ❑ The standard state is identified by specifying a definite pressure (or fugacity), but the temperature is always the same as that of the reaction mixture at equilibrium.
- ❑  $\Delta G^0$  and hence  $K$  will vary with this temperature.
- ❑ For a single species the effect of temperature on its free energy is predicted by Gibbs–Helmholtz equation,

- ❑ 
$$\left( \frac{\partial(G_i/T)}{\partial T} \right)_P = - \frac{H_i}{T^2} \quad 9-22$$

- ❑ For the substance in its standard state, Eq.9-22 can be written as

- ❑ 
$$\left( \frac{d(G_i^0/T)}{dT} \right) = - \frac{H_i^0}{T^2} \quad 9-23$$



# EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

- Multiplying Eq.9-23 by  $\nu_i$  and summing over all species present in the system, we get

$$\left( \frac{d \sum \nu_i G_i^0 / T}{dT} \right) = - \frac{\sum \nu_i H_i^0}{T^2} \quad 9-24$$

- The standard free energy of the reaction and the standard heat of reaction are related to the free energy and enthalpy of individual species respectively as given below:

$$\Delta G^0 = \sum \nu_i G_i^0, \quad \Delta H^0 = \sum \nu_i H_i^0 \quad 9-25$$

- Using these in Eq.9-24 and dividing both sides by R, the following result is obtained

$$\left( \frac{d(\Delta G^0 / RT)}{dT} \right) = - \frac{\Delta H^0}{RT^2} \quad 9-25$$

- Substituting Eq.9-21 into Eq.9-25 yields

$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2} \quad 9-26$$



# EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

- Eq.9-26, known as *van't Hoff equation*, predicts the effect of temperature on the equilibrium constant and hence on the equilibrium yield.
- $\Delta H^0$  in Eq.9-26 is the standard heat of reaction.
- If  $\Delta H^0 < 0$ , i.e. the reaction is exothermic, the equilibrium constant decreases as the reaction temperature increases.
- And for an endothermic reaction, the equilibrium constant will increase with increase in temperature.
- If  $\Delta H^0$ , the standard heat of reaction, is constant, Eq.9-26 on integration yields

- $$\ln \frac{K}{K_1} = - \frac{\Delta H^0}{R} \left( \frac{1}{T} - \frac{1}{T_1} \right) \quad 9-27$$

- $K$  and  $K_1$  are the equilibrium constant values at temperatures  $T$  and  $T_1$  respectively.
- Eq.9-27 may be used to evaluate the equilibrium constant with good results over small temperature ranges.
- The equation is exact if  $\Delta H^0$  is independent of temperature.



# EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

- ❑ A reasonably accurate method of interpolation or extrapolation of equilibrium constant is provided by plotting  $\ln K$  vs  $1/T$ , which leads to a straight line according to Eq.9-27.
- ❑ The variation of the standard heat of reaction with temperature may be taken into account if the molal heat capacities of the various species taking part in the reaction are known as functions of  $T$ .
- ❑ Suppose that the specific heats at constant pressure are expressed as a power function in  $T$ .
- ❑ 
$$C_p = a + bT + gT^2 \quad 9-28$$
- ❑ Then the effect of temperature on the standard heat of reaction may be developed as follows:
- ❑ Since heat of reaction is the enthalpy change between the given initial and final states, it may be evaluated by devising any convenient path between these terminal states for which the enthalpy changes are readily available.
- ❑ Assume that the standard heat at temperature  $T_1$ ,  $\Delta H_{T_1}^0$ , is known and it is desired to calculate the standard heat at temperature  $T$ .

# EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

- The actual reaction occurring at temperature  $T$  for which the heat of reaction is  $\Delta H_{T_1}^0$ , may be treated as occurring along the three paths as depicted in Fig.9-3.

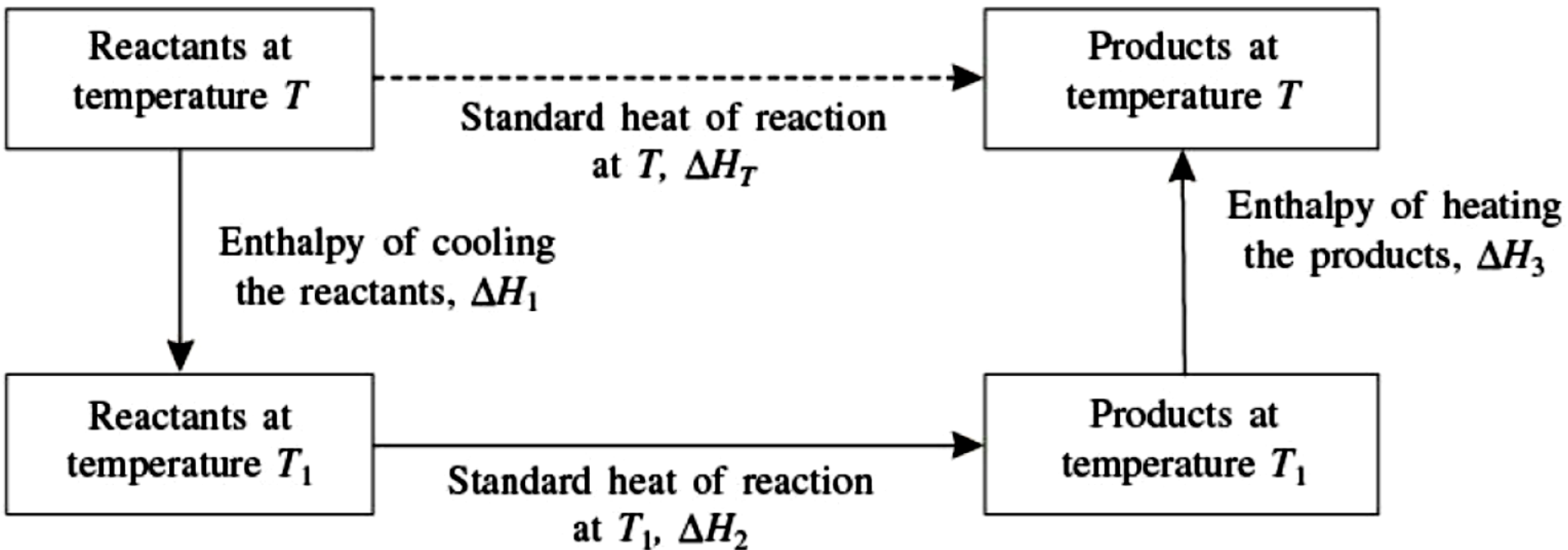


Figure 9-3: Method of estimating the standard heat of reaction at temperature  $T$  given the standard heat of reaction at  $T_1$





# EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

□ From Fig.9-3;

1. The reactants are cooled from temperature  $T$  to  $T_1$ . The enthalpy change for this step is

$$\Delta H_1 = \sum_{\text{Reactants}} \int_T^{T_1} n_i C_{P,i} dT = \sum_{\text{Reactants}} \int_{T_1}^T v_i C_{P,i} dT \quad 9-29$$

2. The reaction is allowed to occur at temperature  $T_1$ . The enthalpy change is

$$\Delta H_2 = \Delta H_{T_1}^0 \quad 9-30$$

3. The temperature of the products is raised from  $T_1$  to  $T$  in this step. The enthalpy change is

$$\Delta H_3 = \sum_{\text{Products}} \int_{T_1}^T n_i C_{P,i} dT = \sum_{\text{Products}} \int_{T_1}^T v_i C_{P,i} dT \quad 9-31$$

□ The standard heat of reaction at temperature  $T$ , is obtained by adding the preceding three equations.

$$\begin{aligned} \Delta H_T^0 &= \Delta H_1 + \Delta H_2 + \Delta H_3 \\ &= \sum_{\text{Reactants}} \int_{T_1}^T v_i C_{P,i} dT + \Delta H_{T_1}^0 + \sum_{\text{Products}} \int_{T_1}^T v_i C_{P,i} dT \end{aligned}$$

# EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

□ The above result can be written as

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \int_{T_1}^T \left( \sum_i v_i C_{P,i} \right) dT \quad 9-32$$

□ The summation in Eq.9-32 is over all the species taking part in the reaction. Using Eq.9-28 in Eq.9-32 yield,

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \int_{T_1}^T \Delta C_P dT \quad 9-33$$

□ Where

$$\Delta C_P = \Delta \alpha + \Delta \beta T + \Delta \gamma T^2 \quad 9-34$$

□ And

$$\Delta \alpha = \sum v_i \alpha_i, \quad \Delta \beta = \sum v_i \beta_i, \quad \Delta \gamma = \sum v_i \gamma_i \quad 9-35$$

□ Eq.9-33 may be expanded to yield the following result.

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \Delta \alpha (T - T_1) + \frac{1}{2} \Delta \beta (T^2 - T_1^2) + \frac{1}{3} \Delta \gamma (T^3 - T_1^3)$$

□ The constants appearing in the above equation can be grouped together to a single constant  $\Delta H^I$  which yields

$$\Delta H_T^0 = \Delta H^I + \Delta \alpha T + \frac{\Delta \beta}{2} T^2 + \frac{\Delta \gamma}{3} T^3 \quad 9-36$$



# EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

- ❑ The constant  $\Delta H^I$  in Eq.9-36 can be evaluated if the heat of reaction at a single temperature is known.
- ❑ Eq.9-36 can then be used for the evaluation of the heat of reaction at any temperature  $T$ .
- ❑ Substitute Eq.9-36 into Eq.9-26 and integrate the resulting expression. The result is

$$\ln K = -\frac{\Delta H'}{RT} + \frac{\Delta\alpha}{R} \ln T + \frac{\Delta\beta}{2R} T + \frac{\Delta\gamma}{6R} T^2 + A \quad 9-37$$

- ❑  $A$  in Eq.9-37 is a constant of integration, which may be evaluated from the knowledge of the equilibrium constant at one temperature.
- ❑ Eq.9-21 relates the equilibrium constant to the standard free energy change.
- ❑ Using this relationship yields

$$\Delta G^0 = \Delta H' - \Delta\alpha T \ln T - \frac{\Delta\beta}{2} T^2 - \frac{\Delta\gamma}{6} T^3 - ART \quad 9-38$$



# EVALUATION OF EQUILIBRIUM CONSTANT

- ❑ Eq.9-37 can be used for the evaluation of the equilibrium constant, provided, we know the dependence of heat capacities on temperature and we also have enough information for the evaluation of the constants  $\Delta H^I$  and  $A$ .
- ❑ Assuming that the heat capacity data are available, the general methods used for the evaluation of the constants  $\Delta H^I$  and  $A$  are listed below.
- ❑ **Method 1.**
  - ❑  $K$  may be calculated from the experimentally measured composition of the equilibrium mixture using Eq.9-10.
  - ❑ If  $K$  values are thus known at two different temperatures, they may be substituted into Eq.9-37.
  - ❑ The resulting two equations are solved for the constants  $\Delta H^I$  and  $A$ .
- ❑ **Method 2.**
  - ❑ Standard heat of reaction at one temperature and one value for the equilibrium constant that is determined by direct experimental measurements are available.
  - ❑ The former is used in Eq. (9.46) for the evaluation of the constant  $\Delta H^I$  and the latter in Eq.9-37 for evaluating the constant  $A$ .



# EVALUATION OF EQUILIBRIUM CONSTANT

## □ Method 3.

- This is the most convenient method since it involves no direct experimental measurements for the equilibrium constant.
- The method makes use of thermal data only, usually in the form of standard heat of reaction  $\Delta H^0$ , and a standard free energy change of reaction  $\Delta G^0$ .
- Then the constants  $\Delta H^I$  and  $A$  are evaluated using Eq.9-36 and Eq. 9-38 respectively.
- $\Delta H^0$  for a reaction may be evaluated from the standard heat of formation,  $\Delta H_f^0$ , that are tabulated for most of the compounds.
- The standard free energy of a reaction can be estimated from the values of standard free energy of formation,  $\Delta G_f^0$  of the various species participating in the reaction and their respective stoichiometric numbers as

$$\Delta G^0 = \sum v_i \Delta G_{i,f}^0 \quad 9-39$$

- Noting that the stoichiometric numbers are positive for the products and negative for the reactants, the above may well be written as

$$\Delta G^0 = \sum_{\text{Products}} |v_i| \Delta G_{i,f}^0 - \sum_{\text{Reactants}} |v_i| \Delta G_{i,f}^0 \quad 9-40$$



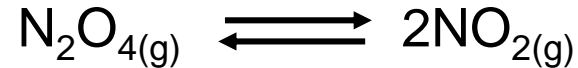
# EVALUATION OF EQUILIBRIUM CONSTANT

- ❑ Thus, the standard free energy of a reaction is the algebraic sum of the free energies of formation of the products minus the algebraic sum of the free energies of formation of the reactants.
- ❑ When an element enters into a reaction, its standard free energy of formation may be taken to be zero.



## **EXAMPLE:**

Calculate the equilibrium constant at 298 K of the reaction



given that the standard free energies of formation at 298 K are 97,540 J/mol for  $\text{N}_2\text{O}_4$  and 51,310 J/mol for  $\text{NO}_2$ .

## **Solution:**

Using Eq.9-40 for the dissociation of  $\text{N}_2\text{O}_4$ ,

$$\begin{aligned}\Delta G^0 &= 2 \times 51,310 - 97,540 \\ &= 5080 \text{ J/mol}\end{aligned}$$

From Eq.9-21,

$$\Delta G^0 = -RT \ln K$$

which gives

$$\ln K = -\frac{\Delta G^0}{RT} = -\frac{5080}{8.314 \times 298} = -2.0504$$

Therefore,  $K = 0.1287$ .



**THANK YOU  
FOR  
YOUR  
ATTENTION!  
ANY QUESTIONS?**