

One of the most important applications of thermodynamics is chemical equilibrium.

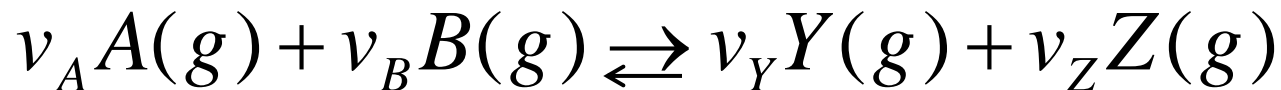
At constant  $T$  and  $P$  (where most chemistry takes place) we know that the condition for equilibrium is  $\Delta G = 0$ .

The sign of  $\Delta G$  dictates whether a process will proceed spontaneously, so if we are not at equilibrium, we can predict which way a reaction will proceed to obtain equilibrium.

We need to apply our thermodynamic knowledge to chemical equilibrium to derive relationships between  $G$  and the equilibrium constant for a chemical reaction.



Start with a gas phase reaction described by a balanced reaction:



Define the *extent of reaction*,  $\xi$  ...

$$\underbrace{n_A}_{\text{Reactants}} = n_{A,0} - \nu_A \xi$$

$$\underbrace{n_Y}_{\text{Products}} = n_{Y,0} + \nu_Y \xi$$

$$n_B = n_{B,0} - \nu_B \xi$$

$$n_Z = n_{Z,0} + \nu_Z \xi$$

$\xi$  varies from 0 to a maximum value dictated by stoichiometry

For example, if  $n_{A,0} = \nu_A$  moles and  $n_{B,0} = \nu_B$  moles, then  $\xi$  varies from...



Recall from the first few [Solutions slides](#)...

At constant  $T$  and  $P$ ,

$$dG = \sum_j \mu_j dn_j = \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z$$

$$dn_A = -\nu_A d\xi \quad dn_B = -\nu_B d\xi \quad dn_Y = \nu_Y d\xi \quad dn_Z = \nu_Z d\xi$$

$$dG = \left( -\nu_A \mu_A - \nu_B \mu_B + \nu_Y \mu_Y + \nu_Z \mu_Z \right) d\xi \quad \text{At constant } T \text{ and } P$$

Book defines  $\Delta_r G$  as the change in Gibbs energy when the extent of reaction changes by one mole. It has units of energy/mol and only has meaning for a specified balanced chemical reaction. (pg 1051)




$$\Delta_r G = \nu_Y \mu_Y + \nu_Z \mu_Z - \nu_A \mu_A - \nu_B \mu_B$$

Eq 24.13  $\mu_j(T, P) = \mu_j^\circ + RT \ln\left(\frac{P_j}{P^\circ}\right)$

Let...  $\Delta_r G^\circ(T) = \nu_Y \mu_Y^\circ(T) + \nu_Z \mu_Z^\circ(T) - \nu_A \mu_A^\circ(T) - \nu_B \mu_B^\circ(T)$

$$\Delta_r G = \Delta_r G^\circ + RT(\nu_Y \ln(P_Y / P^\circ) + \nu_Z \ln(P_Z / P^\circ) - \nu_A \ln(P_A / P^\circ) - \nu_B \ln(P_B / P^\circ))$$

$$\ln \frac{(P_Y / P^\circ)^{\nu_Y} (P_Z / P^\circ)^{\nu_Z}}{(P_A / P^\circ)^{\nu_A} (P_B / P^\circ)^{\nu_B}}$$


Note that  $P^\circ$  is 1 bar in this case and is often not shown in the equation. However, you must remember that there is a reference pressure in the denominator.



$$\Delta_r G = \Delta_r G^\circ(T) + RT \ln Q$$

At equilibrium the Gibbs energy is a minimum wrt any displacement...

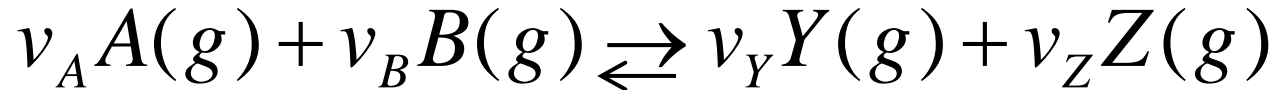
$$\Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{T,P} = 0$$

So ...  $\Delta_r G^\circ(T) = -RT \ln Q_{eq}$

$$\Delta_r G^\circ(T) = -RT \ln K_P(T)$$

Where...  $K_P(T) = \left( \frac{P_Y^{v_Y} P_Z^{v_Z}}{P_A^{v_A} P_B^{v_B}} \right)_{eq}$

The equilibrium constant  
(with the partial pressures at  
their equilibrium values)



Using the ideal gas law,  $P = cRT$ , we can convert  $K_P$  into concentrations

$$K_P(T) = \left( \frac{P_Y^{v_Y} P_Z^{v_Z}}{P_A^{v_A} P_B^{v_B}} \right)_{eq} \xrightarrow{P = cRT} K_P = \frac{c_Y^{v_Y} c_Z^{v_Z}}{c_A^{v_A} c_B^{v_B}} \left( \frac{RT}{P^\circ} \right)^{v_Y + v_Z - v_A - v_B}$$

Add a reference state wrt concentration...

$$K_P = K_c \left( \frac{c^\circ RT}{P^\circ} \right)^{v_Y + v_Z - v_A - v_B} \quad \text{where} \quad K_c = \frac{(c_Y / c^\circ)^{v_Y} (c_Z / c^\circ)^{v_Z}}{(c_A / c^\circ)^{v_A} (c_B / c^\circ)^{v_B}}$$

Often select  $c^\circ$  as 1 mole per liter and don't display it... but don't forget about it!



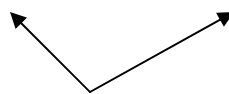
$$\Delta_r G^\circ(T) = -RT \ln K_p(T)$$

One way to find  $\Delta_r G^\circ(T)$ ...

$$\Delta_r G^\circ(T) = \nu_Y \Delta_f G^\circ[Y] + \nu_Z \Delta_f G^\circ[Z] - \nu_A \Delta_f G^\circ[A] - \nu_B \Delta_f G^\circ[B]$$

Another way to find  $\Delta_r G^\circ(T)$ ...

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$



How can you find these?





Initially: 1 mol

0 mol

0 mol

$$K_P(T) = \left( \frac{P_{PCl_3} P_{Cl_2}}{P_{PCl_5}} \right)_{eq}$$

Use  $P_j = x_j P_{tot}$  to find  $P_{eq}$

$$K_P = \frac{\xi_{eq}^2}{1 - \xi_{eq}^2} P$$



# But $K_P$ is only a function of T!

CEq-9

$$K_P = \frac{\xi_{eq}^2}{1 - \xi_{eq}^2} P$$

Looks like a function of  $T$  and  $P$ !

But we know  $K_P$  depends only on  $T$  (see CEq-5)...

Since  $K_P$  is a constant at a fixed temperature, if you have a change in  $P$ , there must be a concomitant change in  $\xi_{eq}$  to maintain the same  $K_P$ .

Remember what this principle is called?!



Following a change in the conditions that displaces equilibrium, a reaction will adjust to new equilibrium state (e.g., changing pressure).



$$K_P = \frac{\xi_{eq}^2}{1 - \xi_{eq}^2} P$$

If I raise  $P$ , what must happen to  $\xi_{eq}$ ?

Figure 26.1





$$G(\xi) = (1 - \xi)\Delta_f G_{N_2O_4}^\circ + 2\xi\Delta_f G_{NO_2}^\circ + (1 - \xi)RT \ln \frac{1 - \xi}{1 + \xi} + 2\xi RT \ln \frac{2\xi}{1 + \xi}$$

So how do I find G( $\xi$ ) at equilibrium?

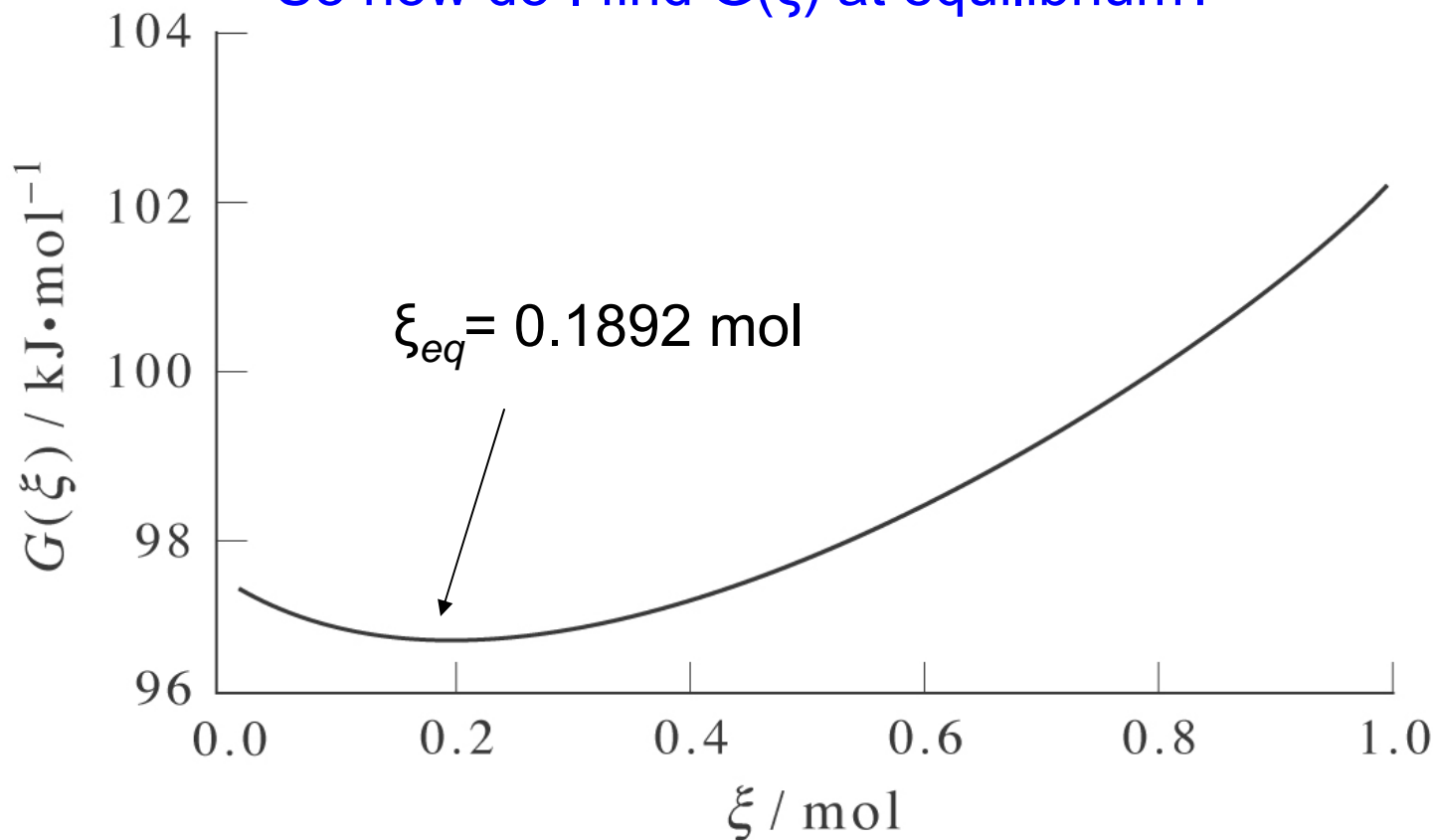


Figure 26.2



Arbitrary pressures

In general:  $\Delta_r G = \Delta_r G^\circ(T) + RT \ln Q_P$

$$Q_P(T) = \left( \frac{P_Y^{v_Y} P_Z^{v_Z}}{P_A^{v_A} P_B^{v_B}} \right)$$

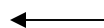
At equilibrium:  $\Delta_r G^\circ(T) = -RT \ln K_P(T)$

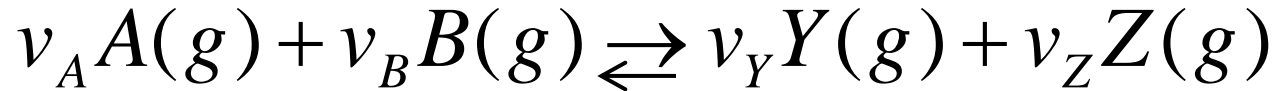
$$K_P(T) = \left( \frac{P_Y^{v_Y} P_Z^{v_Z}}{P_A^{v_A} P_B^{v_B}} \right)_{eq}$$

Equilibrium pressures

Together...

$$\Delta_r G = -RT \ln K_P + RT \ln Q_P$$





$$\Delta_r G = RT \ln \frac{Q_P}{K_P} \quad Q_P = \left( \frac{P_Y^{v_Y} P_Z^{v_Z}}{P_A^{v_A} P_B^{v_B}} \right) \quad K_P = \left( \frac{P_Y^{v_Y} P_Z^{v_Z}}{P_A^{v_A} P_B^{v_B}} \right)_{eq}$$

At equilibrium,  $\Delta_r G = 0$  and  $Q_P = K_P$ .

If  $Q_P < K_P$ , then  $Q_P$  must increase to proceed toward equilibrium.

If  $Q_P > K_P$ , then  $Q_P$  must decrease to proceed toward equilibrium.



# How does $K$ depend on $T$ ?

CEq-14

We can apply the Gibbs-Helmholtz equation

$$\left( \frac{\partial \Delta G^\circ / T}{\partial T} \right)_P = -\frac{\Delta H^\circ}{T^2}$$

And substitute  $\Delta_r G^\circ(T) = -RT \ln K_P(T)$

$$\frac{d \ln K_P(T)}{dT} = \frac{\Delta_r H^\circ}{RT^2} \quad \text{van't Hoff Equation}$$

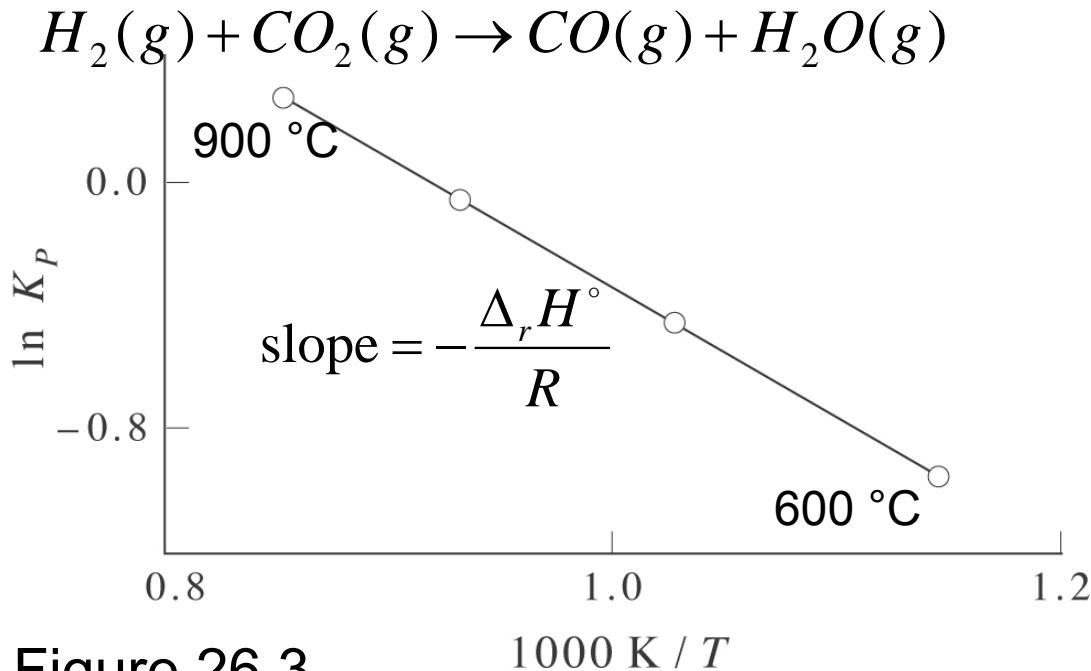
Endothermic:  $\Delta_r H^\circ > 0$      $K_P(T)$     with  $T$ .

Exothermic:  $\Delta_r H^\circ < 0$      $K_P(T)$     with  $T$ .



$$\frac{d \ln K_P(T)}{dT} = \frac{\Delta_r H^\circ}{RT^2} \xrightarrow{\text{Integrate}} \ln \frac{K_P(T_2)}{K_P(T_1)} = \int_{T_1}^{T_2} \frac{\Delta_r H^\circ(T)}{RT^2} dT$$

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = -\frac{\Delta_r H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$



Endothermic or  
Exothermic  
Reaction?

Figure 26.3



If we can't consider  $\Delta_r H(T)$  constant over the temperature range...

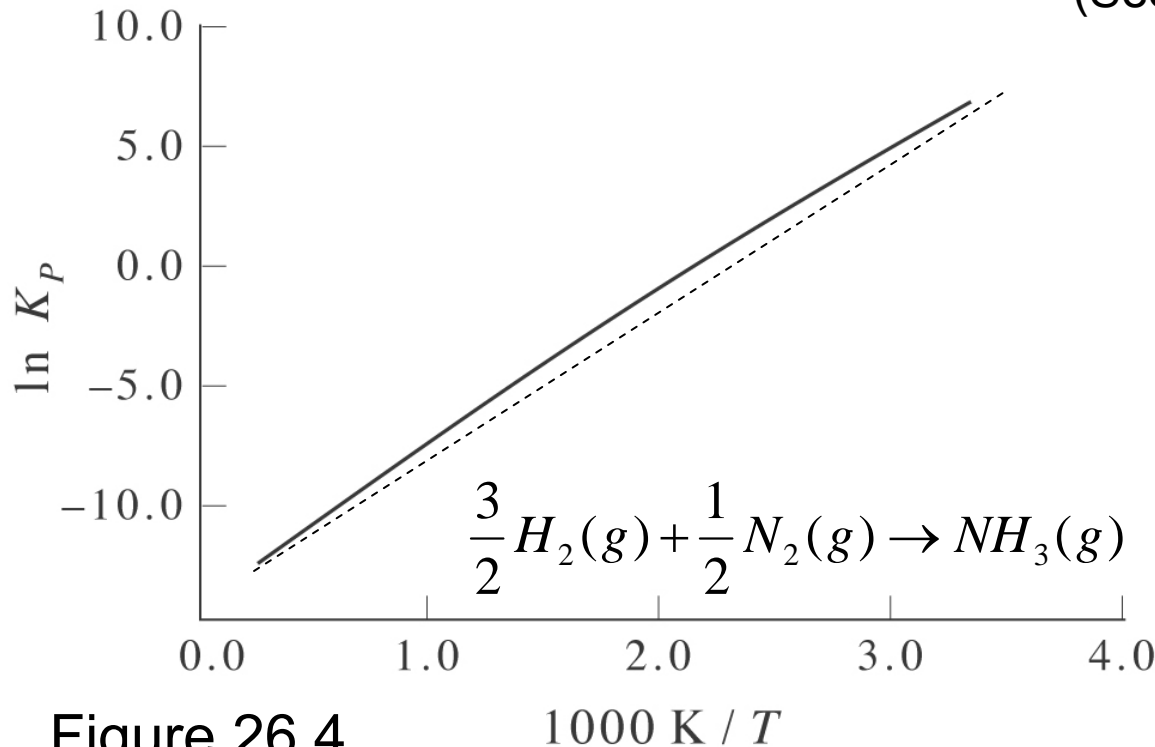
$$\ln \frac{K_P(T_2)}{K_P(T_1)} = \int_{T_1}^{T_2} \frac{\Delta_r H^\circ(T)}{RT^2} dT$$

We know how to calculate temperature dependence of  $\Delta H$ . Recall:

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} C_P^\circ(T) dT$$

Where  $C_p(T)$  is often reported as a series of  $T$  from an experimental fit.  
(See Ex 26-7)

The relationship is no longer linear...

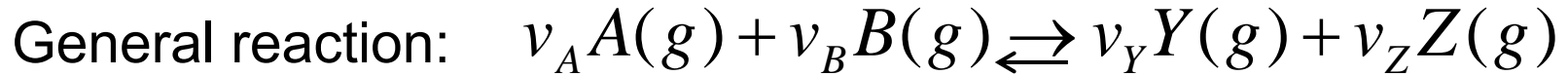


Endothermic or  
Exothermic  
Reaction?

Figure 26.4

1000 K / T





At equilibrium:  $\Delta_r G = v_Y \mu_Y + v_Z \mu_Z - v_A \mu_A - v_B \mu_B = 0$

Recall Partition functions...

$$Q(N_A, N_B, N_Y, N_Z, V, T) = Q(N_A, V, T) Q(N_B, V, T) Q(N_Y, V, T) Q(N_Z, V, T)$$

$$Q(N_A, N_B, N_Y, N_Z, V, T) = \frac{q_A(V, T)^{N_A}}{N_A!} \frac{q_B(V, T)^{N_B}}{N_B!} \frac{q_Y(V, T)^{N_Y}}{N_Y!} \frac{q_Z(V, T)^{N_Z}}{N_Z!}$$

For each constituent...

$$\mu_A = -RT \left( \frac{\partial \ln Q}{\partial N_A} \right)_{N_j, V, T} = -RT \ln \frac{q_A(V, T)}{N_A}$$

Using Stirling's approx for  $N_A!$



# Put it together

CEq-18

$$v_Y \mu_Y + v_Z \mu_Z - v_A \mu_A - v_B \mu_B = 0$$

Insert:  $\mu_A = -RT \ln \frac{q_A(V, T)}{N_A}$

Algebra to get:  $\frac{N_Y^{v_Y} N_Z^{v_Z}}{N_A^{v_A} N_B^{v_B}} = \frac{q_Y^{v_Y} q_Z^{v_Z}}{q_A^{v_A} q_B^{v_B}}$

From definition of  $K_c$ :

$$K_c = \frac{c_Y^{v_Y} c_Z^{v_Z}}{c_A^{v_A} c_B^{v_B}} = \frac{\rho_Y^{v_Y} \rho_Z^{v_Z}}{\rho_A^{v_A} \rho_B^{v_B}} \longrightarrow$$

The equilibrium constant from  
molecular partition functions!





$$K_c = \frac{(q_{HI}/V)^2}{(q_{H_2}/V)(q_{I_2}/V)}$$

Remember from Chapter 18... For an ideal diatomic we have:

$$\frac{q(V, T)}{V} = \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{T}{\sigma \Theta_{rot}} \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}} g_{el} e^{(D_0 + hv/2)/k_B T}$$

$$K_c(T) = \left( \frac{M_{HI}^2}{M_{H_2} M_{I_2}} \right)^{3/2} \left( \frac{4\Theta_{rot}^{H_2} \Theta_{rot}^{I_2}}{(\Theta_{rot}^{HI})^2} \right) \left( \frac{(1 - e^{-\Theta_{vib}^{H_2}/T})(1 - e^{-\Theta_{vib}^{I_2}/T})}{(1 - e^{-\Theta_{vib}^{HI}/T})^2} \right) e^{(2D_0^{HI} - D_0^{H_2} - D_0^{I_2})/RT}$$

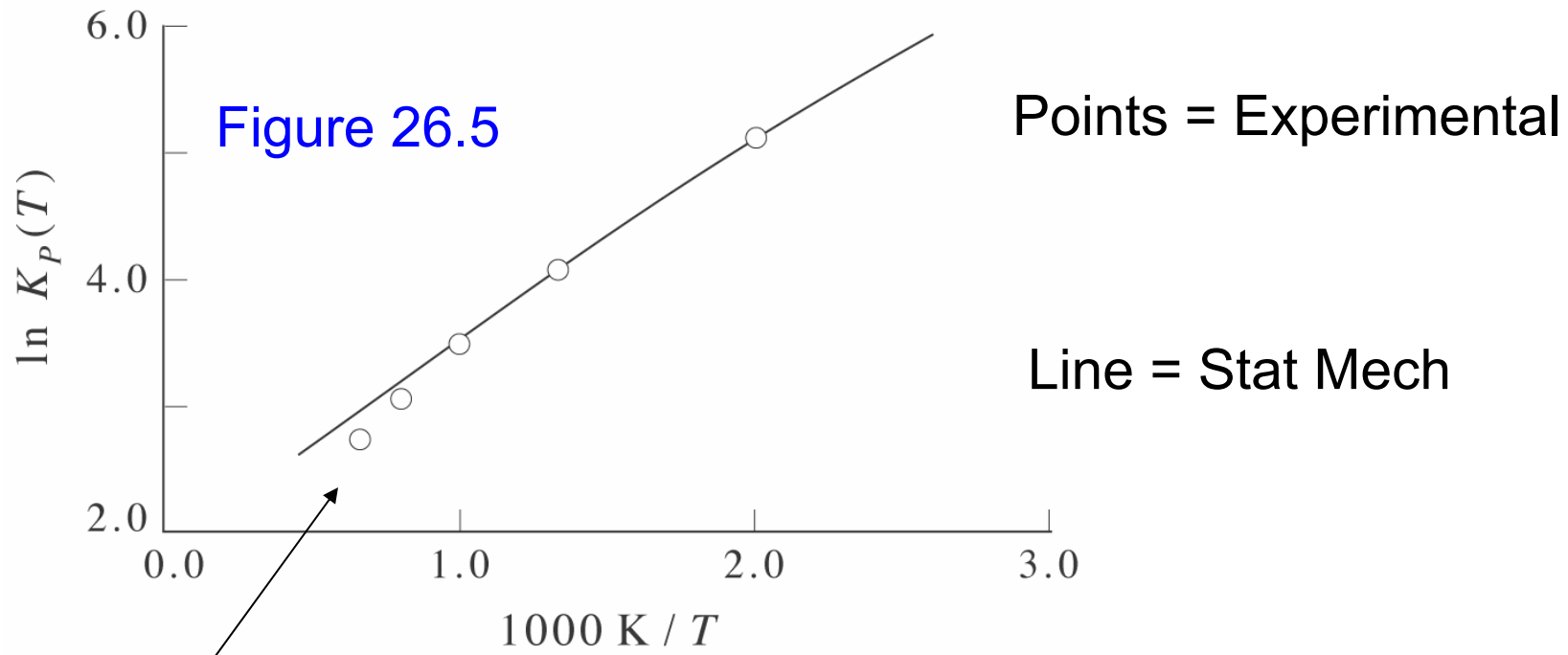
K directly from molecular quantum energy levels!

$$K_P(T) = K_c(T) \left( \frac{c^\circ RT}{P^\circ} \right)^{\nu_Y + \nu_Z - \nu_A - \nu_B}$$





$$K_c(T) = \left( \frac{M_{HI}^2}{M_{H_2} M_{I_2}} \right)^{3/2} \left( \frac{4\Theta_{rot}^{H_2} \Theta_{rot}^{I_2}}{(\Theta_{rot}^{HI})^2} \right) \left( \frac{\left(1 - e^{-\Theta_{vib}^{H_2}/T}\right) \left(1 - e^{-\Theta_{vib}^{I_2}/T}\right)}{\left(1 - e^{-\Theta_{vib}^{HI}/T}\right)^2} \right) e^{(2D_0^{HI} - D_0^{H_2} - D_0^{I_2})/RT}$$



Why the disagreement?



Treatment of chemical equilibrium not so different than gas phase... we just don't use pressures in our equations!

$$\mu = \mu_j^\circ + RT \ln \frac{P_j}{P^\circ}$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q_a$$

$$\Delta_r G^\circ = -RT \ln K_a$$



$$\mu = \mu_j^\circ + RT \ln a_j \quad \text{so} \quad d\mu = RT d \ln a$$

$$d\mu = \bar{V} dP \quad (\text{see Sol-24})$$

$$\bar{V} dP = RT d \ln a$$

$$\int d \ln a_1 = \int_1^{a_1} \frac{1}{a_1} da_1 = \int_{P^\circ=1\text{bar}}^P \frac{\bar{V}}{RT} dP$$



Recall Sol-27 to Sol 29...

$$a = a_{\pm}^{\nu} = (m_{+}^{\nu_{+}} m_{-}^{\nu_{-}})(\gamma_{+}^{\nu_{+}} \gamma_{-}^{\nu_{-}}) \quad \text{On molality scale}$$

$$a = a_{\pm}^{\nu} = (c_{+}^{\nu_{+}} c_{-}^{\nu_{-}})(\gamma_{+}^{\nu_{+}} \gamma_{-}^{\nu_{-}}) \quad \text{On molarity scale}$$

Summary of Table 25.3

$$a_{11} = a_{22} = c^2 \gamma_{\pm}^2 \quad a_{12} = a_{21} = 4c^3 \gamma_{\pm}^3$$

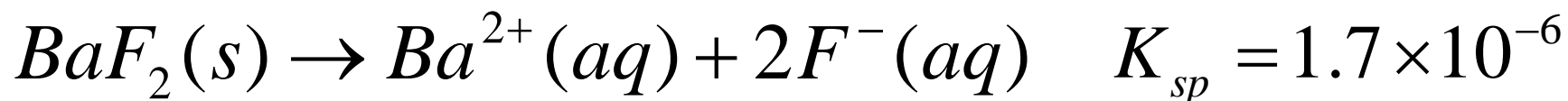
$$a_{13} = a_{31} = 27c^4 \gamma_{\pm}^4$$

What about neutral components?

$$\gamma_{neutral} \approx 1 \quad \text{So...}$$



1. What is the pH at equilibrium for a solution 0.100 M  $\text{CH}_3\text{COOH}$  in water?
2. What is the solubility (i.e., concentration) of  $\text{Ba}^{2+}$  and  $\text{F}^-$  at equilibrium?



- We can use the Gibbs energy to evaluate the position of equilibrium for chemical reactions.
- The Gibbs energy also allows us to understand how chemical systems will respond when displaced from equilibrium (such as changes in pressure and temperature).
- The equilibrium constant can be obtained directly from the partition function.
- Thermodynamic equilibrium constants are expressed in terms of activities – something very important when discussing reactions involving ionic species.

