

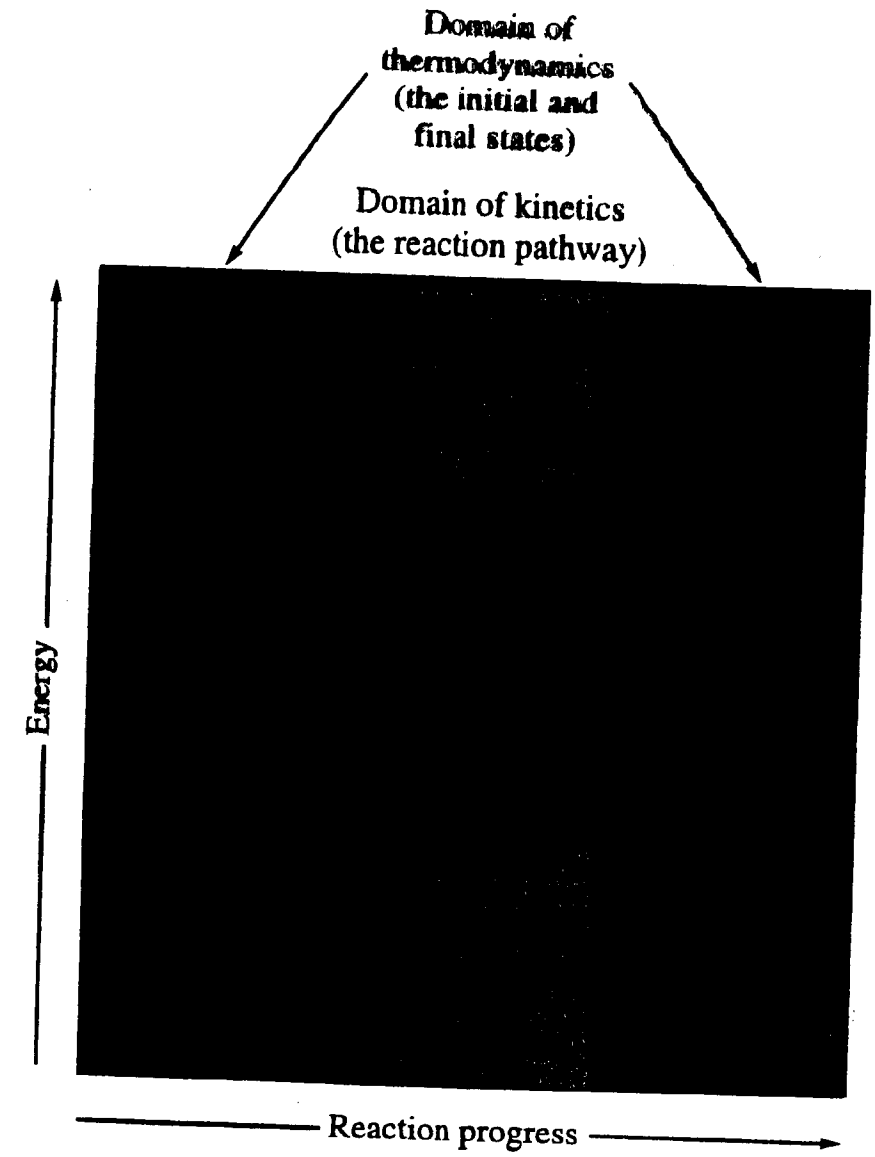
- Entropy
- Entropy and the Second Law of Thermodynamics
- The Effect of Temperature on Spontaneity
- Free Energy ( $\Delta G$ )
- Free Energy and Chemical Reactions
- Free Energy and Equilibrium.

### § 16.1 Spontaneous Processes and Entropy

**Spontaneous process**: An process occurs w/o outside intervention. It may be fast or slow!

see Fig. 16-2

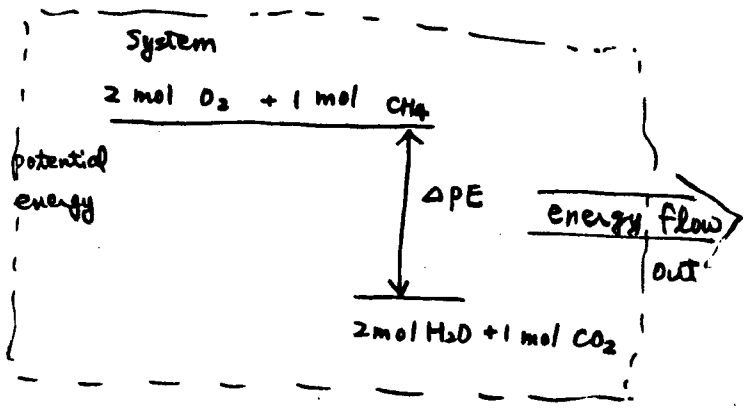
Process 会不会自动发生, 只与反应物与生成物的自由能 (Free Energy) 有关, 与中间过程无关; 但反应速率与中间过程有关。



**Figure 16.2**  
**The domains of kinetics and thermodynamics**  
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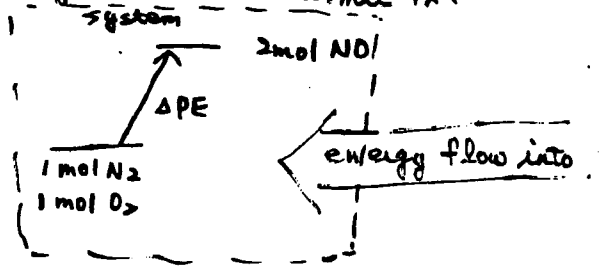
and products (化学组成或化学式) between reactants and products (化学组成或化学式) chemical composition (化学式)

Fig. 6-2 Exothermic rx:



↓  
Energy stored in the chemical bonds is being converted to thermal energy (random kinetic energy) via heat

Fig 6-3 Endothermic rx:



Thermodynamics (热力学): The study of energy and its conversion.

1<sup>st</sup> law of thermodynamics: The energy of the universe is constant.

Internal energy (E): The sum of the kinetic energy and potential energy of all the "particles" in the system.

$$\Delta E = \underset{\substack{\uparrow \\ \text{heat}}}{q} + \underset{\substack{\uparrow \\ \text{work}}}{w}$$

Thermodynamic quantities always consists:

a number: giving the "magnitude" of change

a sign: indicating the "direction" of the flow

exothermic:  $\Delta E < 0$  ( $\because$  system's energy  $\downarrow$ )  
放热

endothermic:  $\Delta E > 0$  ( $\because$  system's energy  $\uparrow$ )  
吸热

$q > 0$  when heat flow from surroundings to system

$q < 0$  when heat flow from system to surroundings

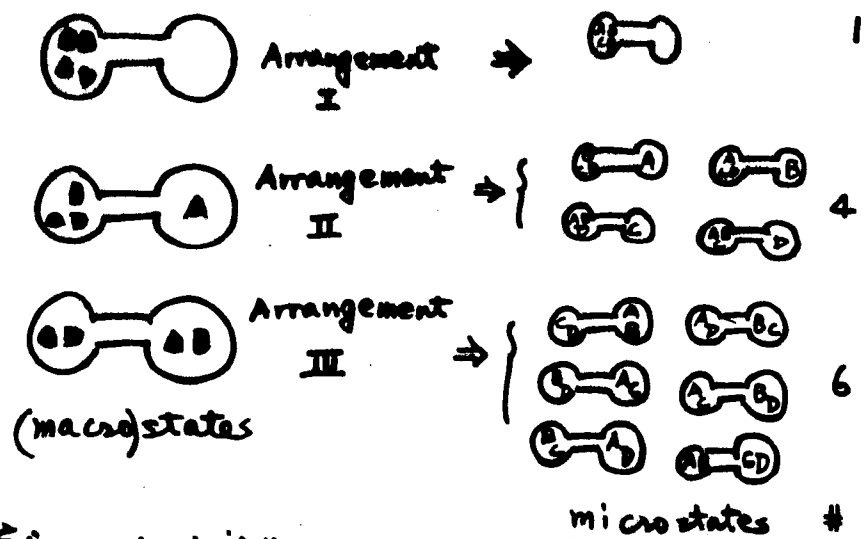
$w > 0$  work done to the system

$w < 0$  work done by the system

$S$ : It can be viewed as a measure of randomness or disorder

Entropy is a thermodynamic function that describes the number of arrangements that are available to a system existing in a given state.

Ex: Fig. 16.4 & Table 16.1



号就 probability (Entropy) 来看, Arrangement III 的机率最大! (视为 1 个 state)

∴ 有 6 种可有的组合 (6 microstates)  
 $S \propto \ln K!$

Positional Probability: it depends on both the number of configurations in space (positional microstates) that yield a particular state.

$$S_{\text{solid}} < S_{\text{liquid}} \ll S_{\text{gas}}$$

• The entropy changes associated w/ the mixing of two pure substances:

↓  
 should be + ( $\Delta S > 0$ )

∴ There are many more microstates for the mixed condition than for the separated condition.

Ex. 16.1 & 16.2

- solid  $\text{CO}_2$  and gaseous  $\text{CO}_2$
- $\text{N}_2$  gas at 1 atm and  $\text{N}_2$  gas at  $1.0 \times 10^{-2}$  atm which has higher positional entropy?

- solid sugar is added to water
- Iodine vapor condenses on a cold surface to form crystals

# Thermodynamics

2<sup>o</sup> law of thermodynamics: In any spontaneous process, there is always an increase in entropy of the universe

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$\Delta S_{\text{universe}} > 0$  for spontaneous process!

$\Delta S_{\text{universe}} = 0$  the process has no tendency to occur. the system is at equilibrium.

$\Delta S_{\text{universe}} < 0$  the process is spontaneous in the opposite direction

## § 16.3 The Effect of Temperature on Spontaneity

Entropy changes in the surroundings:  
for an exothermic process, the heat transferred from the system to the surroundings  
↓  
enhances motion of the molecules in the surroundings

↓  
Increases in disorder at molecular level

↓  
Entropy of the surroundings ↑

Ex. at const pressure, the heat change  
 $\Delta H_{\text{sys}} = q_p$

↓  
 $\Delta S_{\text{surrounding}} \propto \ominus \Delta H_{\text{sys}}$

- For exothermic process:  $\Delta S_{\text{surr}} > 0$
- For endothermic process:  $\Delta S_{\text{surr}} < 0$

If temp is high, the molecules are already energetic. → the absorption of heat from an exothermic process in the system will have little impact on molecular motion  
→ entropy increase will be smaller!

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

- The sign of  $\Delta S_{\text{surr}}$  depends on the direction of the heat flow
- The magnitude of  $\Delta S_{\text{surr}}$  depends on temp



Ex 16.5

At what temp is the following process spontaneous at 1 atm?



ΔH° = 31.0 kJ/mol      ΔS° = 93.0 J/K.mol

What is the normal boiling point of liquid Br<sub>2</sub>?

sol:

ΔG° = ΔH° - TΔS°

at equilibrium (or at boiling point)

ΔG° = 0 = ΔH° - TΔS°

ΔH° = TΔS°

31000 J/mol = T · 93 J/K.mol

T = 333 K

① T < 333 K

② T = 333 K

③ T > 333 K

ΔG° = ΔH° - TΔS° (in J/mol)  
= 3100 - T(93) > 0

ΔG° = 0 right at boiling point

ΔG° < 0 spontaneously boiling

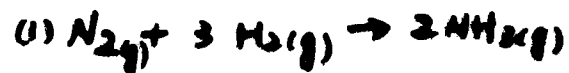
ΔG° = ΔH° - TΔS°      or      ΔS<sub>univ</sub> = ΔS + (-ΔH)/T

16-9

Table 16.5

Case	Result
ΔH negative, ΔS negative	Spontaneous at all temperatures
ΔH positive, ΔS positive endothermic	Spontaneous at high temperatures (where endothermicity is relatively unimportant)
ΔH negative, ΔS negative exothermic	Spontaneous at low temperatures (where exothermicity is dominant)
ΔS negative, ΔH positive	Process not spontaneous at any temperature (reverse process is spontaneous at all temperatures)

16.5 possible combinations of ΔH and ΔS for a process and the resulting dependence of spontaneity on temperature



reactants: 4 molecules

products: 2 molecules

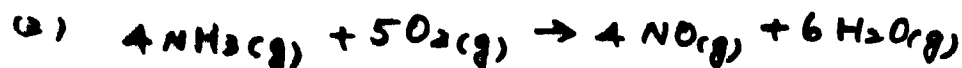
Remember entropy  $\propto$  # of configurations

fewer molecules  $\rightarrow$  fewer configurations

$\therefore \Delta S^\circ < 0$  for this rx.



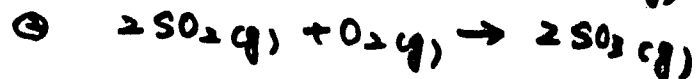
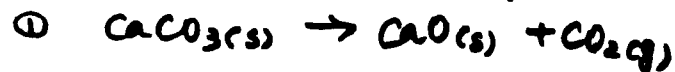
$\Delta S^\circ > 0$



$\Delta S^\circ > 0$

The change in positional entropy is dominated by the relative numbers of molecules of gaseous reactants and products

Ex. 16.6 predict the sign of  $\Delta S^\circ$



sol:  $\textcircled{1}$   $CO_2(g)$  gaseous molecule produced  $\therefore \Delta S^\circ > 0$

$\textcircled{2}$  3 molecules  $\rightarrow$  2 molecules  $\therefore \Delta S^\circ < 0$

3<sup>rd</sup> Law of thermodynamics:

The entropy of a perfect crystal at 0K is zero.  
( $\Delta S^\circ$  at 0K,  $S = 0$  for a perfect crystal)

Standard entropy value ( $S^\circ$ ):

the values represent the increase in entropy that occurs when a substance is heated from 0K to 298K at 1 atm pressure

Ex.  $S^\circ$  of diamond (see Appendix 4, page A21)

$S^\circ = 2 \text{ J/K}\cdot\text{mol}$  (for diamond)

$\therefore$  diamond is highly ordered crystal

$S^\circ = 6 \text{ J/K}\cdot\text{mol}$  (for graphite)

$\therefore$  graphite is H.A. & H.F. -  $\therefore$  disorder

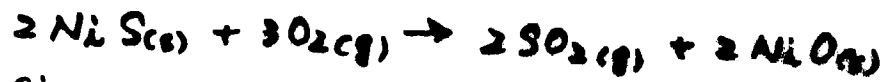
Entropy is a state function of the system (it is not path-dependent)

$$\Delta S^\circ_{\text{reaction}} = \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}}$$

# of moles  
of products

# of moles  
of reactants

Calculate  $\Delta S^\circ$  at  $25^\circ\text{C}$  for the reaction



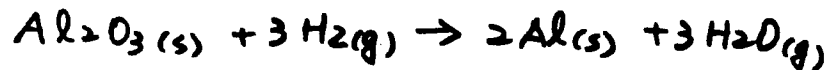
given the following standard entropy values:

Substance	$S^\circ$ (J/K.mol)
$\text{SO}_2(g)$	248
$\text{NiO}(s)$	38
$\text{O}_2(g)$	205
$\text{NiS}(s)$	53

$$\begin{aligned} \text{sol: } \Delta S^\circ &= \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}} \\ &= [2 \times (248) + 2 \times (38)] - [2 \times (53) + 3 \times (205)] \\ &= -149 \text{ J/K} \end{aligned}$$

3 reactants  $\rightarrow$  2 products (2 count # of gaseous molecules)

Ex. 16.8



use the following standard entropy values:

Substance	$S^\circ$
$\text{Al}_2\text{O}_3(s)$	51
$\text{H}_2(g)$	131
$\text{Al}(s)$	28
$\text{H}_2\text{O}(g)$	189

$$\begin{aligned} \Delta S^\circ &= [4(28) + 3(189)] - [2(51) + 3(131)] \\ &= 179 \text{ J/K} \end{aligned}$$

§ 16.6 Free Energy and Chemical Rxns. 16-14

standard free energy changes ( $\Delta G^\circ$ ):  
the change in free energy that will occur if the reactants in their standard states are converted to the products in their standard states.

$\Delta G^\circ$  can not be measured by calorimeter we can use the following equation to calculate  
 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$



$$\Delta H^\circ = -393.5 \text{ KJ}$$

$$\Delta S^\circ = 3.05 \text{ J/K} \quad \Delta G^\circ = ? \text{ at } 298\text{K}$$

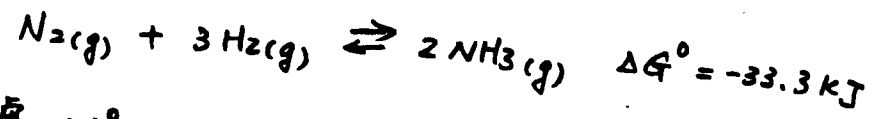
$$\begin{aligned} \text{sol: } \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -393.5 \text{ KJ} - 298^\text{K} \times (3.05 \text{ J/K}) \\ &= -394.4 \text{ KJ} \end{aligned}$$

Ex. 16.9.



Standard free energy change ( $\Delta G^\circ$ ): the change in free energy that will occur if the reactants in their standard states are converted to the products in their standard states

Ex. ammonia synthesis at 25°C



$\Delta G^\circ$  represent the change in free energy when 1 mol  $N_2(g)$  at 1 atm react w/ 3 mol  $H_2(g)$  at 1 atm produce 2 mol  $NH_3(g)$  at 1 atm

\* free energy change of a reaction is not measured directly! ( $\Delta G^\circ$ )

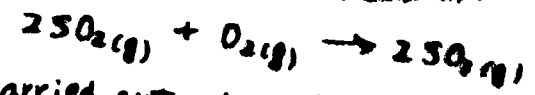
\* Enthalpy ( $\Delta H^\circ$ ) can be measured by calorimeter

There are several ways to calculate  $\Delta G^\circ$

I. Use the equation:

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

consider the reaction:



carried out at 25°C and 1 atm. Calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  using the following data:

Substance	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/K.mol)
$SO_2(g)$	-297	248
$SO_3(g)$	-396	257
$O_2(g)$	0	205

sol:

$$\begin{aligned} \Delta H^\circ &= \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants}) \\ &= 2 \times (-396) - [2 \times (-297) + 0] \\ &= -198 \text{ kJ} \end{aligned}$$

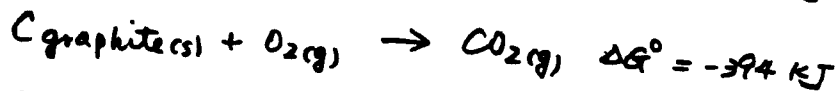
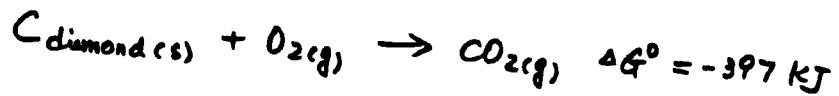
$$\begin{aligned} \Delta S^\circ &= \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}} \\ &= 2 \times 257 - [2 \times (248) + 1 \times 205] \\ &= -187 \text{ J/K} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \quad T = 298 \text{ K} \\ &= -198 \text{ kJ} - 298 \text{ K} \times (-187 \text{ J/K}) \\ &= -142 \text{ kJ} \end{aligned}$$

∴ We can calculate  $\Delta G$  in a similar way to calculate  $\Delta H$  using Hess's Law

Ex. 16.10

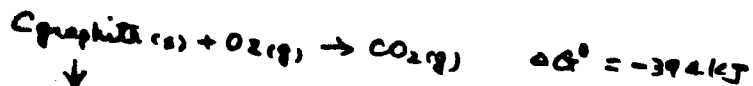
Using the following data (at 25°C)



calculate  $\Delta G^\circ$  for the reaction

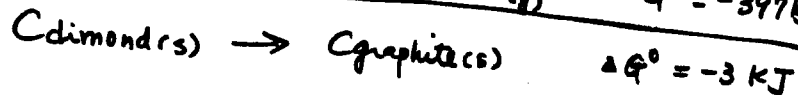
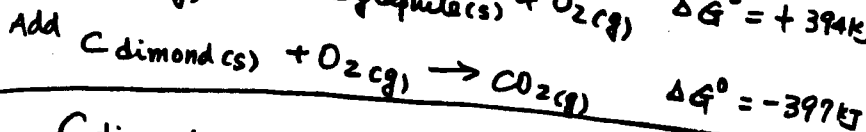
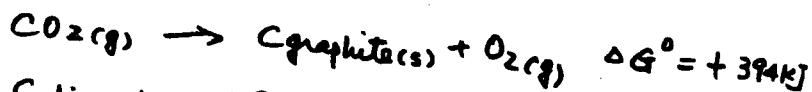


sol:



↓

reversed rx:



$$\therefore \Delta G^\circ < 0$$

∴ Diamond will convert to graphite spontaneously at 25°C (atm. (However, the reaction is very slow))

Using standard free energy of formation to calculate  $\Delta G^\circ$

$$\Delta G^\circ = \sum n_p \Delta G_f^\circ(\text{products}) - \sum n_r \Delta G_f^\circ(\text{reactants})$$

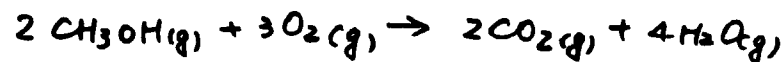
$\Delta G_f^\circ$ : standard free energy of formation

the change in free energy that accompanies the formation of 1 mol of that substance from its constituent elements w/ all reactants and products in their standard states

(The standard free energy of formation of an element in its standard state is zero.)

Ex. 16.11 calculating  $\Delta G^\circ$

Methanol is a high-octane fuel used in high-performance racing engines. Calculate  $\Delta G^\circ$  for the reaction



substance	$\Delta G_f^\circ$ (kJ/mol)
CH <sub>3</sub> OH(g)	-163
O <sub>2</sub> (g)	0
CO <sub>2</sub> (g)	-394
H <sub>2</sub> O(g)	-229

(A) at equilibrium.

$$\begin{cases} Q = K \text{ (equilibrium const)} \\ \Delta G = 0 \end{cases}$$

$$\therefore 0 = \Delta G^\circ + RT \ln K$$

$$\therefore \Delta G^\circ = -RT \ln K$$

$$-\frac{\Delta G^\circ}{RT} = \ln K$$

$$K = e^{-\frac{\Delta G^\circ}{RT}}$$

(B)  $\Delta G < 0$

反應會自發

$\Sigma G_{\text{products}} < \Sigma G_{\text{reactants}}$

(C)  $\Delta G > 0$

"逆反應自發"

Ex. 16.14 > 16.15

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ &= -33.3 + RT \ln \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} \end{aligned}$$

## Free Energy and Equilibrium

### The Temperature Dependence of K

$$\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ$$

$$\begin{aligned} \ln K &= -\frac{\Delta H^\circ}{RT} + \frac{T\Delta S^\circ}{RT} \\ &= -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \end{aligned}$$

at  $T = T_1$

$$\ln K_{T_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_1}\right) + \frac{\Delta S^\circ}{R} \quad \text{--- (1)}$$

at  $T = T_2$

$$\ln K_{T_2} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2}\right) + \frac{\Delta S^\circ}{R} \quad \text{--- (2)}$$

① - ② over a relatively small temp range.

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

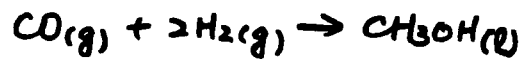
$$\Delta \ln \frac{K_{T_1}}{K_{T_2}} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{--- (3)}$$

van Hoff's equation

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Q: reaction quotient

Ex: 16.13 Calculating  $\Delta G^\circ$



calculate  $\Delta G$  at  $25^\circ\text{C}$  for this rx. where CO at 5.0 atm and  $\text{H}_2$  at 3.0 atm are converted to liquid methanol.

Sol:  $\Delta G = \Delta G^\circ + RT \ln Q$

$$\begin{aligned} \Delta G^\circ &= \Delta G_f^\circ(\text{methanol}) - \Delta G_f^\circ(\text{CO}) - 2\Delta G_f^\circ(\text{H}_2) \\ &= (-166 \text{ kJ}) - (-137 \text{ kJ}) - 2 \times 0 \\ &= -29 \text{ kJ} \rightarrow \text{per mol of CH}_3\text{OH formation} \end{aligned}$$

$$\Delta G = (-29 \text{ kJ/mol}) + RT \ln Q$$

$$Q = \frac{1}{(P_{\text{CO}})(P_{\text{H}_2}^2)} = \frac{1}{5 \cdot (3)^2} = 2.2 \times 10^{-2}$$

$$\begin{aligned} \Delta G &= (-29 \text{ kJ/mol}) + (8.314 \text{ J/K}\cdot\text{mol} \times 298) \cdot \ln(2.2 \times 10^{-2}) \\ &= (-29 \text{ kJ/mol}) + (-94 \text{ kJ/mol}) \\ &= -38 \text{ kJ/mol} \quad \therefore \text{spontaneous rx} \end{aligned}$$

## 16.8 Free Energy and Equilibrium



1.0 mole of gas A is initially placed in a rx vessel at  $p = 2 \text{ atm}$

$$\text{Free Energy of A} = G_A = G_A^\circ + RT \ln(P_A)$$

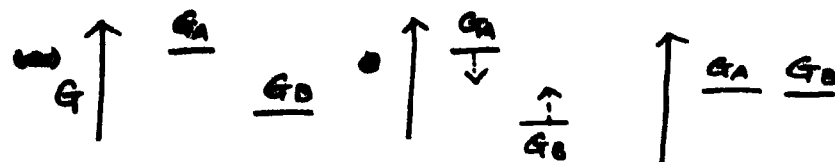
$$\text{" B} = G_B = G_B^\circ + RT \ln(P_B)$$

$$\text{Total free energy of system } G = G_A + G_B$$

(a) initial

(b) start rx

(c) 平衡了



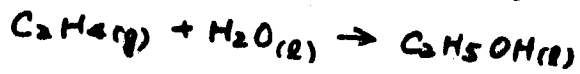
Total free energy



$$\begin{aligned} \Delta G &= G_{\text{product}} - G_{\text{reactant}} \\ &= 0 \\ &\text{at equilibrium} \end{aligned}$$

$$\begin{aligned}
 &= 2 \Delta G_f^\circ(\text{CO}_2) + 4 \Delta G_f^\circ(\text{H}_2\text{O}) - 2 \Delta G_f^\circ(\text{C}_2\text{H}_6) \\
 &\quad - 3 \Delta G_f^\circ(\text{O}_2) \\
 &= 2 \times (-394) + 4 \times (-229) - 2 \times (-67) - 3 \times 0 \\
 &= -1378 \text{ kJ}
 \end{aligned}$$

Ex. 16.12. Free energy and spontaneity  
 A chemical engineer wants to determine the feasibility of making ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) by reacting water w/ ethylene ( $\text{C}_2\text{H}_4$ ) according to the rx:



Is this reaction spontaneous under standard conditions?

Sol: 查表 A.21 (Appendix)

$$\Delta G_f^\circ(\text{C}_2\text{H}_5\text{OH}(\text{l})) = -175 \text{ kJ/mol}$$

$$\Delta G_f^\circ(\text{C}_2\text{H}_4(\text{g})) = 68 \text{ kJ/mol}$$

$$\Delta G_f^\circ(\text{H}_2\text{O}(\text{l})) = -237 \text{ kJ/mol}$$

$$\begin{aligned}
 \Delta G^\circ &= -175 - (68 - 237) \\
 &= -6 \text{ kJ}
 \end{aligned}$$

$\therefore$  The process is spontaneous at  $25^\circ\text{C}$ .

## The Dependence of Free Energy on Pressure

The equilibrium position represents the lowest free energy value available to a particular reaction system.

平衡到達時,  $\Delta G = 0$

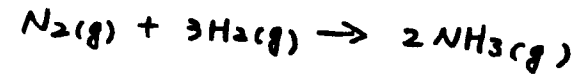
For an ideal gas, enthalpy is not pressure-dependent but entropy is pressure-dependent  
 $G = H - TS$   
 $\therefore$  Free energy is pressure-dependent

$$G = G^\circ + RT \ln(P) \quad \text{for ideal gas}$$

$G^\circ$ : free energy of the gas at a pressure of 1 atm.

$G$ : free energy of the gas at a pressure of  $P_{\text{atm}}$

For a gas reaction, 131+0



$$\Delta G = \sum n_p G_{\text{products}} - \sum n_r G_{\text{reactants}}$$

$$\Delta G = 2 G_{\text{NH}_3} - G_{\text{N}_2} - 3 G_{\text{H}_2}$$

$$= 2 [G_{\text{NH}_3}^\circ + RT \ln P_{\text{NH}_3}] - [G_{\text{N}_2}^\circ + RT \ln P_{\text{N}_2}] - 3 [G_{\text{H}_2}^\circ + RT \ln P_{\text{H}_2}]$$

$$= \{ 2 [G_{\text{NH}_3}^\circ] - G_{\text{N}_2}^\circ - 3 G_{\text{H}_2}^\circ \} + RT \{ \ln P_{\text{NH}_3}^2 - \ln P_{\text{N}_2} - 3 \ln P_{\text{H}_2} \}$$

$$= \Delta G^\circ + RT \ln \left( \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} \right)$$