

Chapter 16: *Spontaneity, Entropy, and Free Energy*

1

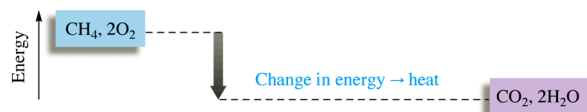
16.1 Spontaneous Processes and Entropy

3

The first law of thermodynamics – the law of conservation of energy:

- Energy can be neither created nor destroyed
- The energy of the universe is constant

Fig. 16.1: When methane and oxygen react to form carbon dioxide and water, the products have lower potential energy than the reactants. This change in potential energy results in energy flow (heat) to the surroundings.



2

Thermodynamics lets us predict **whether a process will occur** but gives no information about the amount of time required for the process.

Kinetics (動力學): focuses on pathways between reactants and products

Thermodynamics (熱力學): considers only the initial and final states

A spontaneous (自發的) process is one that occurs without outside intervention.

4

Fig. 16.2: The rate of a reaction depends on the pathway from reactants to products; this is the domain of kinetics. Thermodynamics tells us whether a reaction is spontaneous based only on the properties of the reactants and products. The predictions of thermodynamics do not require knowledge of the pathway between reactants and products.

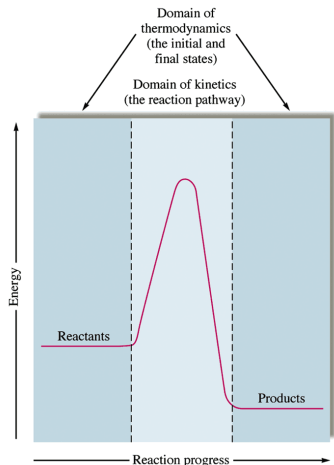
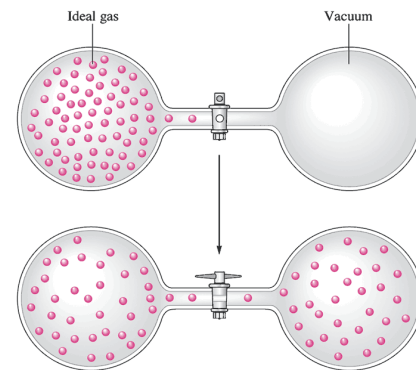


Fig. 16.3: The expansion of an ideal gas into an evacuated bulb.



Entropy (熵、亂度)

The driving force for a spontaneous process is an increase in the entropy of the universe.

Entropy, S , can be viewed as a measure of randomness, or disorder.

Nature spontaneously proceeds toward the states that have the highest probabilities of existing.

Arrangement		Microstates	
	I		
	II		
	III		
	IV		
	V		

TABLE 16.2 Probability of Finding All the Molecules in the Left Bulb as a Function of the Total Number of Molecules

Number of Molecules	Relative Probability of Finding All Molecules in the Left Bulb
1	$\frac{1}{2}$
2	$\frac{1}{2} \times \frac{1}{2} = \frac{1}{2^2} = \frac{1}{4}$
3	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^3} = \frac{1}{8}$
5	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^5} = \frac{1}{32}$
10	$\frac{1}{2^{10}} = \frac{1}{1024}$
n	$\frac{1}{2^n} = \left(\frac{1}{2}\right)^n$
6×10^{23} (1 mole)	$\left(\frac{1}{2}\right)^{6 \times 10^{23}} \approx 10^{-(2 \times 10^{23})}$

9

16.2 Entropy and the Second Law of Thermodynamics

11

Positional Entropy

A gas expands into a vacuum because the expanded state has the highest **positional probability** of states available to the system.

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

Exercise 16.1 & 16.2

10

The second law of thermodynamics:

- In any spontaneous process there is always an increase in the entropy of the universe.
即: $S_{\text{univ}} > 0$ for a spontaneous process.
- The entropy of the universe is increasing.

University = System(系統) + Surrounding(環境)

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

12

16.3 The Effect of Temperature on Spontaneity

13

$$\Delta S_{\text{univ}} = \overset{+}{\Delta S_{\text{sys}}} + \overset{-}{\Delta S_{\text{surr}}}, \text{ 何者為主導決定於 } T$$

於 1 atm 下, if $T > 100\text{ }^\circ\text{C} \Rightarrow$ 則為 spontaneous

if $T < 100\text{ }^\circ\text{C} \Rightarrow$ 則其逆反應自發

Exothermicity is an important driving force for spontaneity. 為 T-dependent [i.e. ΔS_{surr} depends on T at which the energy is transferred.]

例如: 50 J heat transfer, if T 大 \Rightarrow 影響不顯著

T 小 \Rightarrow 影響顯著

(1) The sign ΔS_{surr} depends on the direction of the heat flow.

(2) The magnitude of ΔS_{surr} depends on T .

15

Consider 1 mol $\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{O}_{(g)}$

$\text{H}_2\text{O}_{(l)}$: 18 mL

$\text{H}_2\text{O}_{(g)}$ at 1 atm, $100\text{ }^\circ\text{C}$: $\sim 31\text{ L} \Rightarrow \Delta S_{\text{sys}} > 0$

而對於環境, ΔS_{surr} 主要是由流入/出系統之 heat 決定

For exothermic (放熱) process:

heat flow from 系統 \rightarrow 環境 $\Rightarrow \Delta S_{\text{surr}} > 0$

For endothermic (吸熱) process:

heat flow from 環境 \rightarrow 系統 $\Rightarrow \Delta S_{\text{surr}} < 0$

對上述 $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(g)}$ 而言, $\Delta S_{\text{surr}} < 0$

14

$$\Delta S_{\text{surr}} = (\pm) \frac{\text{quantity of heat (J)}}{\text{temperature (K)}} \begin{pmatrix} \text{exothermic} \\ \text{endothermic} \end{pmatrix}$$

At constant P , $\Delta H = q$

$$\Rightarrow \Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

Exercise 16.3

16

TABLE 16.3 Interplay of ΔS_{sys} and ΔS_{surr} in Determining the Sign of ΔS_{univ}

Signs of Entropy Changes			
ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	Process Spontaneous?
+	+	+	Yes
-	-	-	No (reaction will occur in opposite direction)
+	-	?	Yes, if ΔS_{sys} has a larger magnitude than ΔS_{surr}
-	+	?	Yes, if ΔS_{surr} has a larger magnitude than ΔS_{sys}

17

Free Energy (自由能)

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S \quad (\text{at constant } T, \text{ 由系統的觀點看})$$

A process (at constant T, P) is spontaneous in the direction in which free energy decreases:

$$-\Delta G \text{ means } +\Delta S_{\text{univ}}$$

$$[\Delta G < 0 \Rightarrow \Delta S_{\text{univ}} > 0]$$

19

16.4 Free Energy

18

TABLE 16.4 Results of the Calculation of ΔS_{univ} and ΔG° for the Process $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$ at -10°C , 0°C , and 10°C *

T ($^\circ\text{C}$)	T (K)	ΔH° (J/mol)	ΔS° (J/K · mol)	$\Delta S_{\text{surr}} = -\frac{\Delta H^\circ}{T}$ (J/K · mol)	$\Delta S_{\text{univ}} = \Delta S^\circ + \Delta S_{\text{surr}}$ (J/K · mol)	$T\Delta S^\circ$ (J/mol)	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (J/mol)
-10	263	6.03×10^3	22.1	-22.9	-0.8	5.81×10^3	$+2.2 \times 10^2$
0	273	6.03×10^3	22.1	-22.1	0	6.03×10^3	0
10	283	6.03×10^3	22.1	-21.3	+0.8	6.25×10^3	-2.2×10^2

If ΔH and ΔS favor opposite processes, spontaneity will depend on T

(the exothermic direction will be favored at low T)

20

Effect of ΔH and ΔS on Spontaneity

ΔH	ΔS	Result
-	+	spontaneous at all temps
+	+	spontaneous at high temps
-	-	spontaneous at low temps
+	-	not spontaneous at <u>any</u> temp

Exercise 16.5 21

Apply 2nd law of thermodynamics in chemical reactions

ΔS_{surr} : 由 heat flow that occurs 決定

ΔS_{sys} : 由 position probability 決定 [dominated by relative # of gaseous components]

Exercise 16.6

ΔH (at constant P): 決定反應為 endothermic or exothermic

ΔG (at constant T, P): 決定反應是否為 spontaneous

H, G 之 absolute values cannot be determined

Only $\Delta H, \Delta G$ values can be measured.

23

16.5 Entropy Changes in Chemical Reactions

22

The third law of thermodynamics:

- The entropy of a perfect crystal at 0 K is zero.
即: We can assign absolute entropy values.
(一些物質之 S° at 298 K, 1 atm 列於 Appendix 4.)

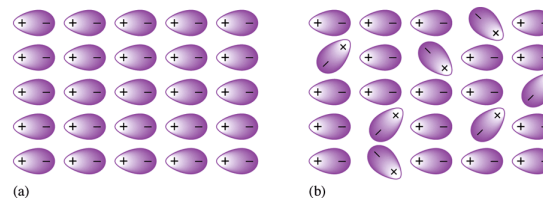
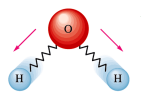


Fig. 16.5: (a) A perfect crystal of hydrogen chloride at 0 K. (b) As the temperature rises above 0 K, lattice vibrations allow some dipoles to change their orientations, producing some disorder and an increase in entropy.

24

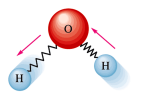
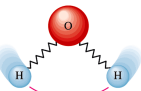


Entropy is a state function of the system:

$$\Delta S^{\circ}_{\text{reaction}} = \sum n_{\text{p}} S^{\circ}_{\text{products}} + \sum n_{\text{r}} S^{\circ}_{\text{reactants}}$$

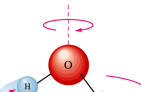
<Entropy is an extensive property.>

Exercise 16.7 & 16.8



Vibrations

Generally, the more complex the molecule, the higher is the standard entropy value (S°).



Rotation

Fig. 16.6: The H_2O molecule can vibrate and rotate in several ways, some of which are shown here.

25

16.6 Free Energy & Chemical Reactions

26

ΔG° : standard free energy change that occurs if reactants in their standard state are converted to products in their standard state.

Note:

- ΔG for a reaction is not measured directly.
- ΔG° 越負，反應越向“ \rightarrow ” to reach equilibrium.

但 G depends on P or *conc.*，須於相同 P or *conc.* 條件下才可由 ΔG 比較反應趨向。

- Remember that ΔG depends on T

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

27

決定 ΔG° 的方法

方法一、 $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ Exercise 16.9

方法二、 使用類似 Hess's law (因為 G 為 state function, 故 ΔG 有加成性) Exercise 16.10

方法三、 使用 ΔG_f°

$$\Delta G^{\circ} = \sum n_{\text{p}} \Delta G_f^{\circ}(\text{products}) - \sum n_{\text{r}} \Delta G_f^{\circ}(\text{reactants})$$

Exercise 16.11 & 16.12

28

16.7 The Dependence of Free Energy on Pressure

29

The meaning of ΔG for a chemical reaction

The system can achieve the lowest possible free energy by going to equilibrium, not by going to completion.

即使一反應 $\Delta G < 0$, 不代表反應完全形成 products

即使一反應 $\Delta G > 0$, 不代表反應完全維持於 reactants

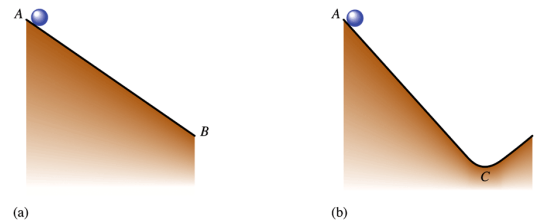


Fig. 16.7: Schematic representations of balls rolling down two types of hills.

31

$$G = G^\circ + RT \ln(P)$$

G° : free energy of the gas at $P = 1$ atm

G : free energy of the gas at $P = P$ atm



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

Q : reaction quotient from the law of mass action.

Exercise 16.13

30

16.8 Free Energy and Equilibrium

32

Equilibrium point: 反應系統可達到之最低自由能的狀態

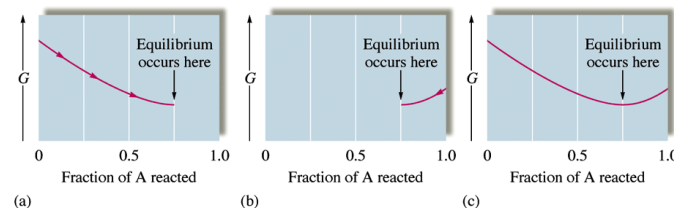
At equilibrium, $Q = K$ and $\Delta G = 0$

$$\Delta G^\circ = -RT \ln(K)$$

K = equilibrium constant

33

Fig. 16.9: (a) The change in free energy to reach equilibrium, beginning with 1.0 mol A(g) at $P_A = 2.0$ atm. (b) The change in free energy to reach equilibrium, beginning with 1.0 mol B(g) at $P_B = 2.0$ atm. (c) The free energy profile for $A(g) \rightleftharpoons B(g)$ in a system containing 1.0 mol (A + B) at $P_{\text{total}} = 2.0$ atm. Each point on the curve corresponds to the total free energy of the system for a given combination of A and B.



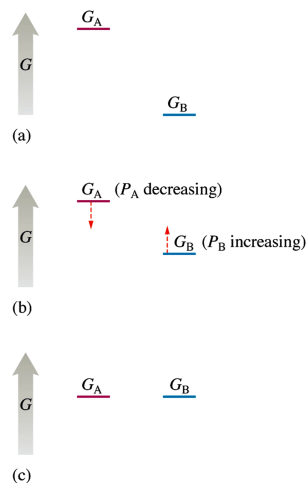
35

Fig. 16.8:

(a) The initial free energies of A and B.

(b) As A(g) changes to B(g), the free energy of A decreases and that of B increases.

(c) Eventually, pressures of A and B are achieved such that $G_A = G_B$, the equilibrium position.



34

TABLE 16.6

Qualitative Relationship Between the Change in Standard Free Energy and the Equilibrium Constant for a Given Reaction

ΔG°	K
$\Delta G^\circ = 0$	$K = 1$
$\Delta G^\circ < 0$	$K > 1$
$\Delta G^\circ > 0$	$K < 1$

Exercise 16.14 & 16.15

36

Temperature Dependence of K

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

$$\Rightarrow \ln(K) = -\frac{\Delta H^\circ}{R} \left(1/T\right) + \Delta S^\circ/R$$

(ΔH° and ΔS° : independent of temperature over a small temperature range)

以 $\ln(K)$ 對 $1/T$ 作圖, slope = $-\Delta H^\circ/R$
y-intercept = $\Delta S^\circ/R$

當 $\Delta H^\circ < 0$, $T \uparrow \Rightarrow K \downarrow$

當 $\Delta H^\circ > 0$, $T \uparrow \Rightarrow K \uparrow$

37

Reversible v. Irreversible Processes

- **Reversible:** The universe is **exactly the same** as it was before the cyclic process.
- **Irreversible:** The universe is **different** after the cyclic process.

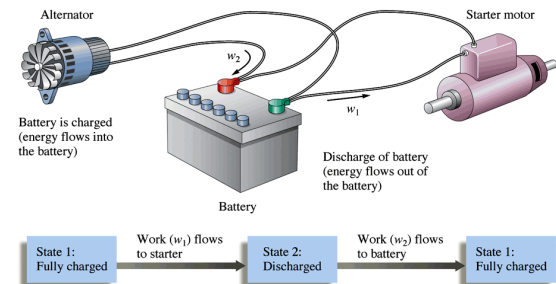
All real processes are irreversible -- (some work is changed to heat, and entropy of the universe increases).

39

16.9 Free Energy and Work

38

Fig. 16.10: A battery can do work by sending current to a starter motor.



- If the current flow in both processes is infinitesimally small, $w_1 = w_2 \Rightarrow$ “reversible process”
- If the current flow is finite, as it would be in any real cases, $w_2 > w_1 \Rightarrow$ “irreversible process”

40

First law: *You can't win. You can only break even.*

Second law: *You can't break even.*

能源 crisis: 由熱力學考量，非關“能源”

⇒ As we use energy, we degrade its usefulness.

所以，we must use these energy sources as wisely as possible.