

## ch 10 The 3<sup>rd</sup> law of Thermodynamics

### 10.1 Statements of 3<sup>rd</sup> law.

3<sup>rd</sup> law 所探討的是 平衡 系統在溫度趨近 0°K 時的性質。

Entropy  $S$  的定義： $S = \int_0^T \frac{\delta Q}{T} + S_0$

其中  $S_0$  (the entropy at absolute zero) 尚未被決定。

Nernst 於 1906 年探討了此問題。

至此所有的問題只討論了 entropy 的差，但這並不表示  $S_0$  就不重要。

例：因  $dG = -SdT + Vdp$ ，欲求  $dG$  就必須知道  $S$ ，  
只知  $dS$  是不夠的。

例：知道絕對的  $S$  值，可算化學反應平衡常數。

固定  $T, P$  下, 系統發生 spontaneous process 的條件:  $G \downarrow$ .

由定義  $G = H - TS$ , 又由 reciprocity relation  $S = -\left(\frac{\partial G}{\partial T}\right)_P$

$$\Rightarrow G = H + T\left(\frac{\partial G}{\partial T}\right)_P \quad (10.2)$$

若系統等溫, 定壓由 initial state  $\rightarrow$  final state:

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \quad (10.3)$$

由 (10.2), (10.3)  $\Rightarrow$  at  $0^\circ K$ :  $\begin{cases} G = H \\ \Delta G = \Delta H \end{cases}$  上式看出

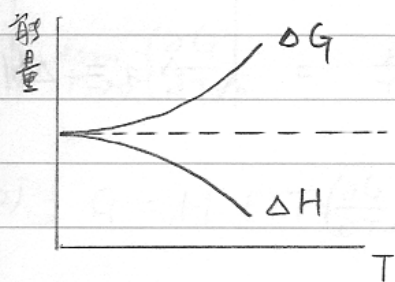


Fig 10.1

Based on the results of experiments, Nernst postulated that as the temperature tends zero, not only do  $\Delta G$  and  $\Delta H$  become equal, but their temperature rates of change approach zero as well:

由實驗結果  
猜測出

$$\lim_{T \rightarrow 0} \left[ \frac{\partial(\Delta G)}{\partial T} \right]_P = 0 ; \quad \lim_{T \rightarrow 0} \left[ \frac{\partial(\Delta H)}{\partial T} \right]_P = 0. \quad (10.4)$$

$$\Rightarrow \lim_{T \rightarrow 0} \left[ \frac{\partial(\Delta G)}{\partial T} \right]_P = \lim_{T \rightarrow 0} \left[ \left( \frac{\partial G_2}{\partial T} \right)_P - \left( \frac{\partial G_1}{\partial T} \right)_P \right] = 0. \quad (10.5)$$

$$= \lim_{T \rightarrow 0} (S_1 - S_2) = 0 \quad (10.6)$$

Nernst formulation of the 3rd law:

All reactions in a liquid or solid in thermal equilibrium take place with no change of entropy in the neighborhood of absolute zero.

實際上, It is believed to hold for all systems in equilibrium state

1911, Planck 推廣了 Nernst 的 hypothesis.

$$\text{由 } \left[ \lim_{T \rightarrow 0} G(T) = \lim_{T \rightarrow 0} H(T) \right] \Rightarrow \left[ \lim_{T \rightarrow 0} (G-H) = 0 \right] \quad (10.7)$$

$$\text{又 } \left[ \lim_{T \rightarrow 0} \left( \frac{\partial G}{\partial T} \right)_P = \lim_{T \rightarrow 0} \left( \frac{\partial H}{\partial T} \right)_P \right] \Rightarrow \left[ \lim_{T \rightarrow 0} \left[ \frac{\partial (G-H)}{\partial T} \right]_P = 0 \right] \quad (10.8)$$

$$\text{由 (10.2)} \quad G = H + T \left( \frac{\partial G}{\partial T} \right)_P$$

$$\Rightarrow -T \left( \frac{\partial H}{\partial T} \right)_P = T \left[ \frac{\partial (G-H)}{\partial T} \right]_P - (G-H)$$

$$\text{設 } \Phi = G-H \Rightarrow T \left( \frac{\partial \Phi}{\partial T} \right)_P - \Phi = -T \left( \frac{\partial H}{\partial T} \right)_P$$

$$\Rightarrow \left( \frac{\partial \Phi}{\partial T} \right)_P - \frac{\Phi}{T} = - \left( \frac{\partial H}{\partial T} \right)_P \quad (10.11)$$

By L'Hôpital rule: the limit of  $\frac{\Phi}{T} \xrightarrow{T \rightarrow 0} 0$  for  $T=0$  is the same as the limit of  $\left( \frac{\partial \Phi}{\partial T} \right)_P$ . 則 (10.11)  $\Rightarrow \lim_{T \rightarrow 0} \left( \frac{\partial H}{\partial T} \right)_P = 0$

$$\Rightarrow \lim_{T \rightarrow 0} \left( \frac{\partial H}{\partial T} \right)_P = 0 \quad \xrightarrow{\text{再由 (10.8)}} \lim_{T \rightarrow 0} \left( \frac{\partial G}{\partial T} \right)_P = 0 \quad (10.13)$$

$$\Rightarrow \lim_{T \rightarrow 0} S = 0 \quad (10.14)$$

Planck's statement of the 3<sup>rd</sup> law:

The entropy of a true equilibrium state of a system at absolute zero is zero.

有些物質 (如 glass) at  $0^\circ\text{K}$ , 其  $S \neq 0$ , 這是因為 glass 是 disorder.

對於純物質 at  $0^\circ\text{K}$ ,  $S=0$  均成立.

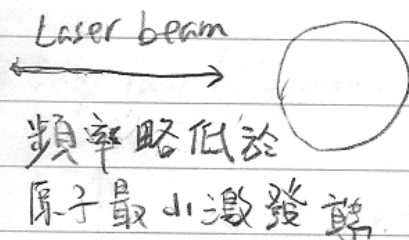
8 - 3<sup>rd</sup> law statement

It is impossible to reduce the temperature of a system to absolute zero using a finite number of processes.

## 10.2 Methods of Cooling

① 早期的, 使系統絕熱, 再用絕熱可逆過程.

② 1970s, Laser cooling



←○→  
向左走的原子因 Doppler shift, 可吸收光子, 向右走的幾乎不吸收. 受激原子向各方向均勻輻射光子, 淨效應是原子減速而降溫.

Laser Cooling 方法更進步, 目前可降到  $\mu\text{K}$  以下.

### 10.3 Equivalence of the statements

要證明 3<sup>rd</sup> law 的兩種說法是相同的

① At 0°K  $S=0$ , ② 有限數量的過程不可能達到 0°K.

由②

We assume that the absolute zero is unattainable, and prove that at 0°K the change from equilibrium state 1 to equilibrium state 2 :

$$\Delta S_0 \equiv S_{0,2} - S_{0,1} = 0$$

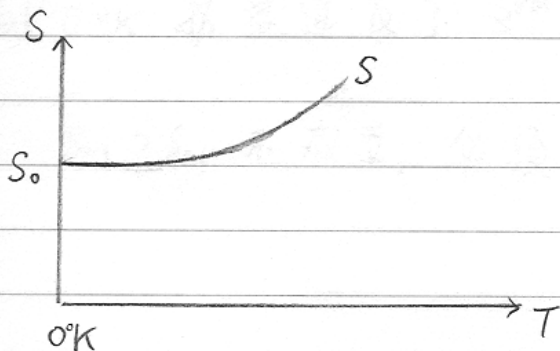
$$\text{已知 } S = S_0 + \int_{T=0}^T \frac{\delta Q_r}{T}$$

↑  
0K時系統 entropy

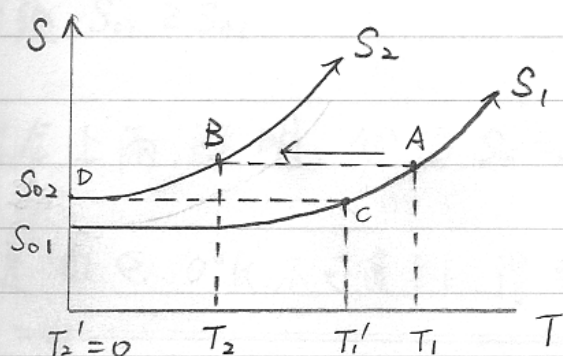
因  $C_p = \left(\frac{\delta Q}{dT}\right)_p$ ,  $C_v = \left(\frac{\delta Q}{dT}\right)_v$ , 在固定 P, V 下:  $C = C_p = C_v$

$$\Rightarrow S = S_0 + \int_{T=0}^T C \frac{dT}{T}$$

由 Debye law (Chapter 16.3),  $C_v \propto T^3$  for a solid.



先設  $S_{02} > S_{01}$ ，然後證明其不成立。



Cooling from  $T_1$  to  $T_2$  by an adiabatic (isentropic) reversible process: 由  $A \rightarrow B$  水平線。

$$\text{因 } A, B \text{ 兩點的 } S \text{ 相同} \Rightarrow S_{02} + \int_0^{T_2} C_2 \frac{dT}{T} = S_{01} + \int_0^{T_1} C_1 \frac{dT}{T}$$

$$\Rightarrow \int_0^{T_2} C_2 \frac{dT}{T} = -(S_{02} - S_{01}) + \int_0^{T_1} C_1 \frac{dT}{T}$$

因本討論之前題是  $S_{02} > S_{01} \Rightarrow S_{02} - S_{01} > 0$

又  $C_1$  及  $C_2$  大於 0。

$$\Rightarrow \text{必可找到 } -T_1' \text{ 使 } \int_0^{T_1'} C_1 \frac{dT}{T} - (S_{02} - S_{01}) = 0.$$

$$\text{亦即存在 } -T_2' \text{ 使 } \int_0^{T_2'} C_2 \frac{dT}{T} = 0 \Rightarrow \text{必然 } T_2' = 0^\circ\text{K}$$

如此即可由 an adiabatic (isentropic) reversible process 從  $C \rightarrow D$  達到  $0^\circ\text{K}$ 。這違反了 3rd law:  $0^\circ\text{K}$  不可經達到 with 有限 process.

$\Rightarrow S_{02} > S_{01}$  不成立，必須  $S_{02} \leq S_{01}$ 。

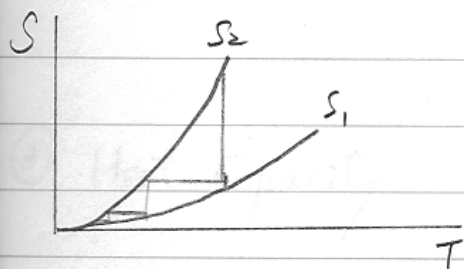


若改為假設  $S_{01} > S_{02}$ , 則經由相同的方法可證得它不成立,  
必須  $S_{02} \geq S_{01}$

綜上兩證明, 必須  $S_{01} = S_{02}$ .

是由  $\textcircled{2}$   $0^\circ\text{K}$  不可達到 得到  $\textcircled{1}$   $\lim_{T \rightarrow 0} (S_1 - S_2) = 0 \Rightarrow \lim_{T \rightarrow 0} S = 0$ .

由 Fig 10.4 可知, 一連串絕熱與等溫交互使用, 可使  $T \rightarrow 0^\circ\text{K}$   
但達不到  $0^\circ\text{K}$ .



#### 10.4 Consequences of 3<sup>rd</sup> Law.

① Volume expansion  $\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$  Maxwell relation  $\frac{1}{V} \left( \frac{\partial S}{\partial P} \right)_T$

因  $\lim_{T \rightarrow 0} \left( \frac{\partial S}{\partial P} \right)_T = 0 \Rightarrow \lim_{T \rightarrow 0} \beta = 0$ .

## ② Slope of the phase transformation curves

由 (Sec 8.7) Clausius - Clapeyron eq.:  $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$  (8.28)

因 Nernst law (3rd law)  $\lim_{T \rightarrow 0} \Delta S \rightarrow 0$

$\Rightarrow \lim_{T \rightarrow 0} \frac{dP}{dT} = 0$  The slope of the boundary between two phases is zero at absolute zero.

此在 Helium II to solid helium 間  $\frac{dP}{dT} \propto T^2$  得到證明.

## ③ Heat Capacity

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V$$

$$C_P = T \left( \frac{\partial S}{\partial T} \right)_P$$

積分  
 $\Rightarrow$

$$\underbrace{S - S_0}_{\text{有限}} = \int_0^T \underbrace{\frac{C_V}{T}}_{\infty \text{ at } 0K} dT$$

$$\underbrace{S - S_0}_{\text{有限}} = \int_0^T \underbrace{\frac{C_P}{T}}_{\infty \text{ at } 0K} dT$$

$$\Rightarrow \lim_{T \rightarrow 0} C_V = 0$$

$$\lim_{T \rightarrow 0} C_P = 0$$