

4-1 自由能



重點提示

1. 自由能即為G (Gibbs free energy) , 及A (Helmholtz free energy) 。

2. 反應起始時, 為自發不可逆狀態 $\Rightarrow TdS > dQ$

反應終止時, 為平衡可逆狀態 $\Rightarrow TdS = dQ$

將兩者結合, 得 $TdS \geq dQ$, 即為Clausius Inequality

在熱力學第一定律中, $dQ = dU - dW$

代入得 $TdS \geq dU - dW$ 或 $-dU + dW + TdS \geq 0$

3. 在定溫及定壓系統下:

$$-dU + dW + TdS \geq 0$$

$$\Rightarrow -dU - PdV + TdS \geq 0$$

因為 $dP = 0$, $PdV = d(PV)$

$$dT = 0, TdS = d(TS)$$

$$\Rightarrow -[dU + d(PV) - d(TS)] \geq 0$$

定義 $G = H - TS = U + PV - TS$

$$\Rightarrow -dG \geq 0$$

得 $dG \leq 0$ 或 $\Delta G \leq 0$, 即一反應要自發進行, 其G值要不斷下降, 直到下降至一最小值, 此時 $\Delta G = 0$, 此時反應達到平衡。

4. 在定溫系統下:

$$-dU + dW + TdS \geq 0$$

$$\Rightarrow -dU - PdV + TdS \geq 0$$

因為 $dT = 0$, $TdS = d(TS)$

$$\Rightarrow -d(U - TS) \geq PdV$$

定義 $A = U - TS$

$$\Rightarrow -dA \geq PdV$$

得 $-dA \geq dW$ 或 $-\Delta A \geq W$, 即在恆溫過程中, 系統所作的最大功恰為其流失之A值。

補充說明

G與A間之關係式為 $G = A + PV$, 類似 $H = U + PV$ 。



4-4 物理化學經典題型解析

5. $dG = -SdT + VdP$

在定溫時， $dG = VdP$

$$\Rightarrow \int dG = \int_{P^\circ}^P VdP$$

$$\Rightarrow \boxed{G = G^\circ + \int_{P^\circ}^P VdP}$$

P° 為一大氣壓，故 G° 為 the standard Gibbs free energy。

(1) 對固或液體而言，其在反應過程中，體積變化不大，可視為定值：

$$\text{故 } G = G^\circ + \int_{P^\circ}^P VdP$$

$$\Rightarrow G = G^\circ + V(P - P^\circ)$$

(2) 對理想氣體而言：

$$G = G^\circ + \int_{P^\circ}^P VdP$$

$$\Rightarrow G = G^\circ + \int_{P^\circ}^P \frac{nRT}{P} dP$$

$$\Rightarrow \boxed{G = G^\circ + nRT \ln P}$$

定義 u (potential energy) = $\frac{G}{n}$

$$\boxed{u = u^\circ + RT \ln P}$$

範例 1



For the process $A \rightarrow B$, the value ΔG is 30KJ at 25°C , and 30.02KJ at 26°C . Estimate ΔS for the process. (89成大化學)

Sol:

需 G vs. S 之關係式

$$dG = -SdT + VdP$$

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

$$\Rightarrow \left(\frac{\partial \Delta G}{\partial T} \right) = -\Delta S$$

$$\begin{aligned}\Rightarrow \Delta S &\doteq -\frac{\Delta G(299\text{K}) - \Delta G(298\text{K})}{299 - 298} \\ &= -\frac{30.02 - 30}{299 - 298} \\ &= -0.02\text{KJ/K或} -20\text{J/K}\end{aligned}$$

範例(2)



Show that, for a transition between two incompressible solid phase, ΔG is independent of the pressure. (89交大應化)

Sol:

需G vs. P之關係式

$$\begin{aligned}dG &= -SdT + VdP \\ \Rightarrow \left(\frac{\partial G}{\partial P}\right) &= V \\ \Rightarrow \left(\frac{\partial \Delta G}{\partial P}\right) &= \Delta V\end{aligned}$$

因incompressible $\Rightarrow \Delta V = 0$

即 $\left(\frac{\partial \Delta G}{\partial P}\right) = 0 \Rightarrow \Delta G$ 和P無關

範例(3)



The molar Gibbs free energy of a gas is given by $G = RT \ln(P/P_0) - (a + bT + c/T)P$, where P_0 is a standard pressure and a, b, c are constants.

- (1) Derive an expression for the molar entropy of the gas.
- (2) Derive an expression for the molar heat capacity, C_p , of the gas.
- (3) Derive the equation of state for the gas. (90台大化學)

Sol:

$$\begin{aligned}(1) dG &= -SdT + VdP \\ \Rightarrow \left(\frac{\partial G}{\partial T}\right)_p &= -S\end{aligned}$$

- (1) Derive an expression for the compression factor $Z = 1 + aP + bP^2 + \dots$, i.e., Virial series in terms of pressure, assuming βP is very small ($\ll 1$). What is the value of a and b , respectively.
- (2) Obtain the analytic function of fugacity as a function of β and P .
(hint: $\ln f = \ln P + \frac{1}{RT} \int_0^P \left[V_m - \frac{RT}{P} \right] dP$) (95中央化學)

Sol:

$$(1) PV(1 - \beta P) = RT \Rightarrow \frac{PV}{RT} = \frac{1}{1 - \beta P}$$

$$\text{其中 } Z = \frac{PV}{RT} \quad \& \quad \frac{1}{1 - \beta P} = 1 + \beta P + (\beta P)^2 + \dots, \text{ 若 } \beta P \ll 1$$

$$\Rightarrow Z = 1 + \beta P + (\beta P)^2 + \dots = 1 + aP + bP^2 + \dots$$

$$\text{得 } a = \beta, \quad b = \beta^2$$

$$(2) PV(1 - \beta P) = RT \Rightarrow V = \frac{RT}{P} \cdot \frac{1}{1 - \beta P} = \frac{RT}{P} \cdot [1 + \beta P + (\beta P)^2 + \dots]$$

$$\text{因 } \beta P \text{ 很小} \Rightarrow V \text{ or } V_m \doteq \frac{RT}{P} \cdot (1 + \beta P)$$

$$\text{代回 } \ln f = \ln P + \frac{1}{RT} \int_0^P \left[V_m - \frac{RT}{P} \right] dP = \ln P + \frac{1}{RT} \int_0^P \left[\frac{RT}{P} \cdot (1 + \beta P) - \frac{RT}{P} \right] dP$$

$$\Rightarrow \ln f = \ln P + \int_0^P \beta dP$$

$$\Rightarrow \ln \frac{f}{P} = \beta P$$

$$\text{得 } f = P \cdot \exp(\beta P)$$

綜合練習

1. For reaction $\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$

$$\Delta_f G(\text{N}_2\text{O}_4, g) = +97.89 \text{ kJ/mol}; \Delta_f H(\text{N}_2\text{O}_4, g) = +9.16 \text{ kJ/mol};$$

$$\Delta_f G(\text{NO}_2, g) = +51.31 \text{ kJ/mol}; \text{ and } \Delta_f H(\text{NO}_2, g) = +33.18 \text{ kJ/mol at } 298 \text{ K.}$$

(1) Calculate the equilibrium constant of the reaction at 298 K.

4-30 物理化學經典題型解析

(2)若0.1 mol之 A_2 氣體在30°C下，裝填於3公升之容器中。當反應達到平衡時，總壓為1.2 atm。試求其解離度 α = ? 平衡常數 K_p = ?

(96專利商標審查人員特考)

36. 氣相化學反應 $C_2H_{4(g)} + H_{2(g)} \rightleftharpoons C_2H_{6(g)}$ 之平衡常數 K_p 和溫度 T 有如下之關係 $\ln K_p(\text{bar}) = \frac{-14.51 + 16471}{T(\text{K})}$ ，試求：

- (1) 此反應在 1090 K，1 bar 標準狀況下之焓 (enthalpy $\Delta_{\text{rxn}}H^\circ$)，熵 (entropy $\Delta_{\text{rxn}}S^\circ$)，吉勃士自由能 (Gibb's free energy $\Delta_{\text{rxn}}G^\circ$)。假設 $\Delta_{\text{rxn}}H^\circ$ 、 $\Delta_{\text{rxn}}S^\circ$ 和溫度無關，氣體常數 $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1} = 0.082 \text{ bar } \lambda\text{K}^{-1}\text{mol}^{-1}$ 。
- (2) 假設所有反應物和生成物均為理想氣體，以一莫耳 C_2H_4 和一莫耳 H_2 在 1090 K 定溫及 1 bar 定壓下進行化學反應，達平衡時生成物 C_2H_6 有幾莫耳？
- (3) 同上小題(2)，若是在 1090 K，180 升之定容下反應，達平衡時生成物 C_2H_6 有幾莫耳？ (90簡任升等)

練習解析

1. (1) $\Delta G_{\text{rxn}}^\circ = 2 \times 51.31 - 97.89 = 4.73 \text{ kJ/mol}$ 或 4730 J/mol

代入 $\Delta G_{\text{rxn}}^\circ = -RT \ln K_p$
 $\Rightarrow 4730 = -8.314 \times 298 \times \ln K_p$

得 $K_p = 0.148$ (at 298K)

(2) $\Delta H_{\text{rxn}}^\circ = 2 \times 33.18 - 9.16 = 57.2 \text{ kJ/mol}$ or 57200 J/mol

代入 $\ln \frac{K_{p2}}{K_{p1}} = -\frac{\Delta H^\circ}{R} \times \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

$\Rightarrow \ln \frac{K_{p2}}{0.148} = -\frac{57200}{8.314} \times \left(\frac{1}{343} - \frac{1}{298} \right)$

得 $K_p = 3.06$ (at 70°C 或 343K)