化学反应和热力学平衡态

$$aA + bB \xrightleftharpoons{T.P给定} cC + dD \qquad \xi = \frac{-dn_A}{a} = \frac{-dn_B}{b} = \frac{dn_C}{c} = \frac{dn_D}{d}$$

$t=0$ $\quad n_A^0 \quad n_B^0 \quad n_C^0 \quad n_d^0$

$t=t$ $\quad n_A^0 - a\xi \quad n_B^0 - b\xi \quad n_C^0 + c\xi \quad n_d^0 + d\xi$

反应物 ν_i $-$

生成物 ν_i $+$

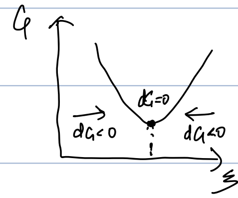
$$G = \sum_i \mu_i n_i = \sum_i \mu_i (n_i^0 + \nu_i \xi)$$

考虑溶剂和载体 $\quad G = \sum_i \mu_i (n_i^0 + \nu_i \xi) + \sum_{不变量} \mu_k n_k = f(\xi, \mu_1, \cdots, \mu_c)$

T.P给定 $\quad dG = \sum_i \mu_i \nu_i d\xi + \sum_i (n_i^0 + \nu_i \xi) d\mu_i + \sum_{不变量} \mu_k dn_k$

吉布斯-杜亥姆公式， $\sum n_i d\mu_i = 0$ $\quad \therefore dG = \sum_i \mu_i \nu_i d\xi$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \sum_i \mu_i \nu_i \begin{cases} =0 & 平衡 \\ \neq 0 & 未平衡 \end{cases}$$



$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \sum_{\substack{i \\ 产物}} \mu_i \nu_i - \sum_{\substack{j \\ 反应物}} \mu_j \nu_j = \Delta_r G$$

反应吉布斯自由能

(强度性质)

(不是偏摩尔量)

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

化学平衡常数

$$K = \left.\frac{\alpha_C^c \cdot \alpha_D^d}{\alpha_A^a \cdot \alpha_B^b}\right|_{平衡}$$

平衡时 $\quad \Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{T,p} = 0$

$$\mu_i = \mu_i^0 + RT \ln \alpha_i$$

$$\mu_i^0 \begin{cases} 气态 & \ominus & \frac{p_i}{p^\ominus} & 标准态 \ (100kPa) \\ 溶液 & * & \alpha_i & 纯态 \ (不约束压强) \end{cases}$$

平衡时 $\quad \sum_i \nu_i \mu_i = \sum_i \nu_i (\mu_i^0 + RT \ln \alpha_i) = 0$

$$-\sum_i \nu_i \mu_i^0 = RT \sum_i \nu_i \ln \alpha_i$$

$$\sum \ln \alpha_i^{\nu_i} = -\frac{1}{RT} \sum_i \nu_i \mu_i^0$$

$$K = \prod_i \alpha_i^{\nu_i} = e^\wedge\left(-\frac{\sum \nu_i \mu_i^0}{RT}\right) \quad 为常数$$

$$\sum_i \nu_i \mu_i^0 \triangleq \Delta_r G^0 \quad 标准反应吉布斯自由能$$

$$\therefore K = e^{\left(-\frac{\Delta_r G^\circ}{RT}\right)} \qquad \Delta_r G^\circ = -RT\ln K$$

$\alpha_i = \gamma_i x_i \quad \therefore K = \prod_i \gamma_i^{\nu_i} \cdot \prod_i x_i^{\nu_i}$

$$\Delta_r G = \Delta_r G^\circ + RT\ln\prod_i \alpha_i^{\nu_i} \qquad \overset{\text{非平衡}}{\Omega} = \prod_i \alpha_i^{\nu_i}\ \text{反应活度积}$$

$$= RT\ln\frac{\Omega}{K}$$

平衡常数 K 与 T、P 关系

i. P不变，K随T变化

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \left(\frac{\partial\left(-\frac{\Delta_r G^\circ}{RT}\right)}{\partial T}\right)_p = -\left(\frac{1}{RT}\cdot\left(\frac{\partial \Delta_r G^\circ}{\partial T}\right)_p + \Delta_r G^\circ\cdot\left(\frac{\partial\left(\frac{1}{RT}\right)}{\partial T}\right)_p\right)$$

$$= \frac{\Delta_r S^\circ}{RT} + \frac{\Delta_r G^\circ}{RT^2} = \frac{\Delta_r H^\circ}{RT^2}$$

反应 吸热，$\Delta_r H^\circ > 0$　　T↑ K↑

放热、　<0　　T↑ K↓

ii T不变，K随P变化

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = \left(\frac{\partial\left(-\frac{\Delta_r G^\circ}{RT}\right)}{\partial p}\right)_T$$

$\begin{cases} \text{气态}\quad \Delta_r G^\circ \text{ — } \overset{\text{标准态}}{p^\ominus} \text{ 与P无关} \\ \text{溶液}\quad * \quad \text{会与P有关} \end{cases}$

K的计算

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

$$\begin{tikzcd} A + B \arrow[rr, "\Delta G^\circ"] & & C + D \\ & C.H.O\cdots \arrow[ul, "\Delta G"] \arrow[ur, "\Delta G"'] & \end{tikzcd}$$

最稳定单质

$\Delta_f G^\circ$

标准吉布斯生成能

$$\Delta_r G^\circ = \underbrace{\sum_i \nu_i \Delta_f G_i}_{\text{产物}} - \underbrace{\sum_j \nu_j \Delta_f G_j}_{\text{反应物}}$$

化学平衡与混合

理想气体的简单反应　　$A(g) \underset{}{\overset{T.P}{\rightleftharpoons}} B(g)$

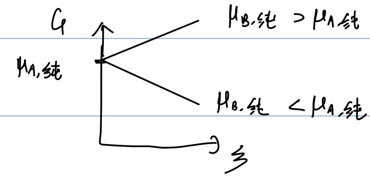
$t=0 \quad n_0 \qquad 0$

$p \qquad t=0 \quad n_0-\xi \qquad \xi$

$A(g) \rightarrow A(g),\ B(g)$（分离态）$\rightarrow A+B\ (g)$（混合态）

分离态 $G_{分离} = (n_0-\xi)\mu_{A,纯} + \xi\mu_{B,纯}$

$= n_0\mu_{A,纯} + \xi(\mu_{B,纯} - \mu_{A,纯})$



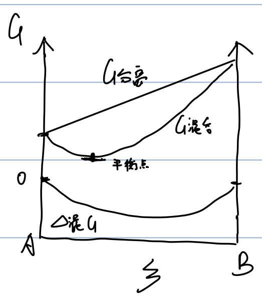
$G_{混合} = (n_0-\xi)\mu_A + \xi\mu_B$

$= (n_0-\xi)\left(\mu_A^\ominus + RT\ln\frac{p_A}{p^\ominus}\right) + \xi\left(\mu_B^\ominus + RT\ln\frac{p_B}{p^\ominus}\right)$

$G_{分离} = (n_0-\xi)\left(\mu_A^\ominus + RT\ln\frac{p}{p^\ominus}\right) + \xi\left(\mu_B^\ominus + RT\ln\frac{p}{p^\ominus}\right)$

$G_{混合} = G_{分离} + (n_0-\xi)RT\ln\frac{p_A}{p} + \xi\cdot RT\ln\frac{p_B}{1}$

$= G_{分离} + \underbrace{(n_0-\xi)RT\ln x_A + \xi RT\ln x_B}_{\Delta_{混}G}$



$\Delta_{混}G = n_0\left[RT\ln\left(1-\frac{\xi}{n_0}\right) + \frac{\xi}{n_0}RT\ln\frac{\xi/n_0}{1-\xi/n_0}\right]$

异相反应

i　所有物种都以纯的凝聚态出现　　$C_{石墨} \xrightarrow{T.P} C_{金刚石}$

$\Delta_r G = \Delta_r G^\circ \begin{cases} T.P\ 特殊点，可能=0, & G^\circ_{产物} = G^\circ_{反应物}，有平衡，没有平衡常数 \\ 可能\ \neq 0，没有平衡 \end{cases}$

ii　涉及气相的异相反应　　$CaCO_3 \xrightarrow{T.P} CaO + CO_2\uparrow$

$\Delta_r G = \mu_{CO_2} + \mu_{CaO} - \mu_{CaCO_3} = \mu^\ominus_{CO_2} + RT\ln\frac{p_{CO_2}}{p^\ominus} + \mu^*_{CaO} - \mu^*_{CaCO_3}$

$= \Delta_r G^\circ + RT\ln\frac{p_{CO_2}}{p^\ominus}$

平衡时 $-\Delta_r G^\circ = RT\ln \boxed{\frac{p_{CO_2}}{p^\ominus}}$ $=K$ 有平衡和K

iii 涉及混合物的异相反应 $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO_4^{3-}{}_{(aq)}$

$\Delta_r G = \Delta_r G^\circ + RT\ln a_{Ca^{2+}}^{\nu_{Ca^{2+}}}\cdot a_{PO_4^{3-}}^{\nu_{PO_4^{3-}}}$

平衡时 $-\Delta_r G^\circ = RT\ln \boxed{a_{Ca^{2+}}^{\nu_{Ca^{2+}}}\cdot a_{PO_4^{3-}}^{\nu_{PO_4^{3-}}}} = K_{sp}$

平衡常数的性质

1. K无量纲

2、不同形式的K $K = K_\gamma \cdot K_x$ 若 $K_\gamma \approx$ 常数 则 $K_x \approx$ 常数

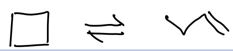
mol/L $K_{[i]} = \underset{\text{单位校正}}{B}\ K_x$

化学平衡常数与统计热力学

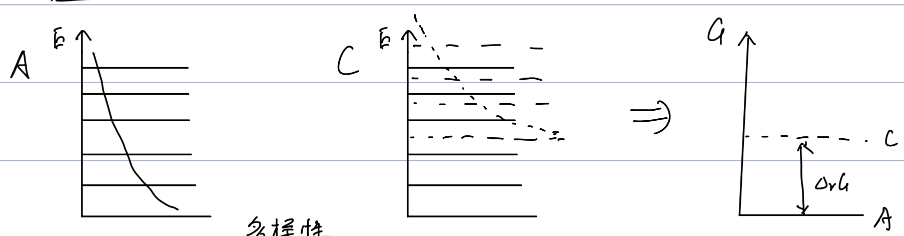
玻尔兹曼 $A \overset{T,P}{\rightleftharpoons} C$

概率比 $\frac{P_C}{P_A} = e^\wedge\left(-\frac{\Delta E}{RT}\right) = \frac{x_C}{x_A}\Big|_{平衡}$

$K = \frac{x_C}{x_A}\Big|_{平衡} = e^\wedge\left(\frac{-\Delta_r G^\circ}{RT}\right)$ $\Delta_r G^\circ = \Delta_r E^\circ + P\Delta_r V^\circ - T\Delta_r S^\circ$



$\Delta_r S^\circ > 0$ $\Delta_r V^\circ$ 变化很小 $\Delta_r G^\circ \neq \Delta E$



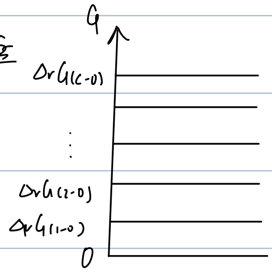
多样性

将S(多样性)包涵G中

反应因子 $K = \frac{p_{产物}}{p_{反应物}} = \frac{x_{产物}}{x_{反应物}} = \boxed{e^\wedge\left(\frac{-\Delta_r G^\circ}{RT}\right)}$ 反应因子

平衡常数：元素在不同电子态的分布

多重产物反应

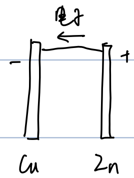


$C + 2H_2O \longrightarrow CO_2 + 2H_2$ Ⅰ

$C + 2H_2O \longrightarrow CO + H_2O + H_2$ Ⅱ

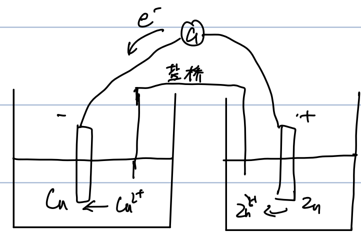
电子态 $[C+2H_2O]$、$[CO_2+2H_2]$、$[CO+H_2O+H_2]$

电化学

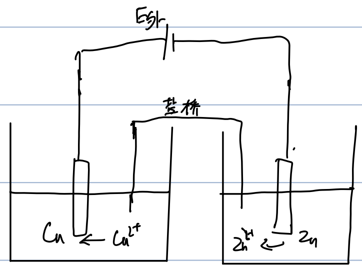


$\mu_{电子,Zn} > \mu_{电子,Cu}$

带+，↓ 带−，↑



外接电源后



当 $\Delta E \to 0$ 电池可逆

可逆电化学

化学反应 ⟷ 电化学

$$dG \le -dW_{非} = -dW_{电}$$

可逆/平衡时 $dG = -dW_{电}$

$Cu^{2+} + 2e^- = Cu$ $Zn = Zn^{2+} + 2e^-$

$Cu^{2+} + Zn = Zn^{2+} + Cu$

T.P恒定 $dG = \left(\frac{\partial G}{\partial \xi}\right)_{T,P} \cdot d\xi = \Delta_r G \cdot d\xi$

$\therefore \Delta_r G = -\nu F E$

$dW_{电,可逆} = -Eq = -E \cdot \underbrace{\nu}_{电荷转移数} \cdot F \cdot d\xi$

若 $\Delta_r G = 0$，达到平衡时 $E = 0$ ≠ 可逆

标准态 $\Delta_r G^\circ = -\underbrace{E^\circ}_{标准电池电势} \nu F = -RT \ln K$ $E^\circ = \frac{RT}{\nu F} \ln K$

$\Delta_r G = \Delta_r G^\circ + RT \ln \Omega$ $E = E^\circ - \frac{RT}{\nu F} \ln \Omega$ 能斯特方程

$-E\nu F = -E^\circ \nu F + RT \ln \Omega$

E° 与 T、P 关系

$$\left(\frac{\partial E^\circ}{\partial T}\right)_p = -\frac{1}{\nu F}\left(\frac{\partial \Delta_r G^\circ}{\partial T}\right)_p = \frac{\Delta_r S^\circ}{\nu F}$$

$$\Delta_r H^\circ = \Delta_r G^\circ + T\Delta_r S^\circ = -\nu F E^\circ + T\nu F\frac{dE^\circ}{dT}$$

$$= \nu F\left(T\frac{dE^\circ}{dT} - E^\circ\right)$$

$$\left(\frac{\partial E^\circ}{\partial P}\right)_T = -\frac{1}{\nu F}\left(\frac{\partial \Delta_r G^\circ}{\partial P}\right)_T \approx 0$$

电极反应和电极电势　　　电极电势

正极　$Cu^{2+} + 2e^- = Cu$　　$E^\circ_{Cu^{2+}/Cu}$

负极　$Zn^{2+} + 2e^- = Zn$　　$E^\circ_{Zn^{2+}/Zn}$

$E^\circ = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn}$

参照　$Pt|\underset{1\,bar}{H_2}|\underset{1\,mol\cdot L^{-1}}{H^+}$　　$E^\circ = 0$

氢气电极

电池电动势测定

对消、补偿法 —— 可逆条件

电解质溶液热力学

$NaCl + H_2O$　　Na^+, Cl^-, H_2O

$$\mu_{Na^+} = \left(\frac{\partial G}{\partial n_{Na^+}}\right)_{T,P,n_{Cl^-},n_{H_2O}}$$

但 Na^+ 和 Cl^- 有联系，不好处理

$$\mu_{NaCl} = \left(\frac{\partial G}{\partial n_{NaCl}}\right)_{T,P,n_{H_2O}}$$

$$dG = \mu_{NaCl}\,dn_{NaCl} + \mu_{H_2O}\,dn_{H_2O}$$

$$dG = \mu_{Na^+}\,dn_{Na^+} + \mu_{Cl^-}\,dn_{Cl^-} + \mu_{H_2O}\,dn_{H_2O}$$

$$= (\mu_{Na^+} + \mu_{Cl^-})\,dn_{NaCl} + \mu_{H_2O}\,dn_{H_2O}$$

$\therefore \mu_{NaCl} = \mu_{Na^+} + \mu_{Cl^-}$

$$\mu_i = \mu_i^\circ + RT\ln a_i$$

$$\mu_{Na^+} = \mu_{Na^+}^\circ + RT\ln a_{Na^+}$$

$$\mu_{Cl^-} = \mu_{Cl^-}^\circ + RT\ln a_{Cl^-}$$

$$\mu_{NaCl} = \underbrace{\mu_{Na^+}^{\circ} + \mu_{Cl^-}^{\circ}}_{= \mu_{NaCl}^{\circ}} + RT\ln a_{Na^+} a_{Cl^-}$$

NaCl 平均活度 $a_{NaCl,\pm} = \sqrt{a_{Na^+} a_{Cl^-}}$

德拜-休克尔理论