

$$\delta p = \left(\frac{\partial p}{\partial v}\right)_T \delta v + \left(\frac{\partial p}{\partial T}\right)_v \delta T$$

$$\delta s = \left(\frac{\partial s}{\partial v}\right)_T \delta v + \left(\frac{\partial s}{\partial T}\right)_v \delta T$$

$$\Rightarrow \left[\left(\frac{\partial p}{\partial v}\right)_T \delta v + \left(\frac{\partial p}{\partial T}\right)_v \delta T \right] \delta v - \delta T \left[\left(\frac{\partial s}{\partial v}\right)_T \delta v + \left(\frac{\partial s}{\partial T}\right)_v \delta T \right] < 0$$

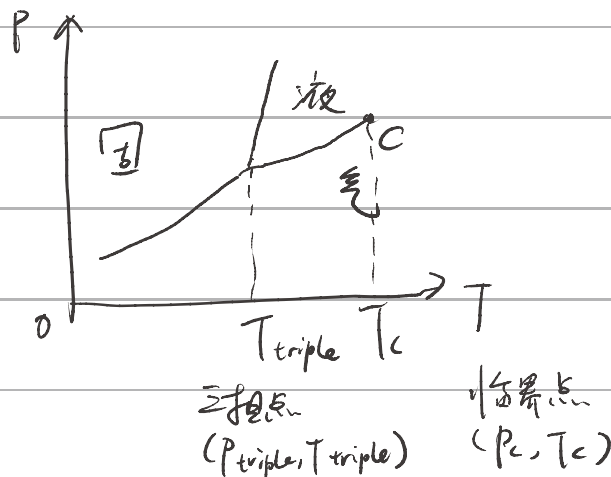
$$\Rightarrow \left(\frac{\partial s}{\partial T}\right)_v \delta T^2 - \left(\frac{\partial p}{\partial v}\right)_T \delta v^2 \geq 0 \Rightarrow \frac{C_v}{T} \delta T^2 + \frac{1}{v K_T} \delta v^2 \geq 0.$$

$$\frac{C_v}{T} - \frac{1}{2 K_T}$$

$$\Rightarrow C_v \geq 0, K_T \geq 0.$$

相图, 克拉珀龙方程.

两相平衡条件: $\mu^\alpha(T, p) = \mu^\beta(T, p)$



$$d\mu^\alpha = -s^\alpha dT + v^\alpha dp$$

$$d\mu^\beta = -s^\beta dT + v^\beta dp$$

$$\Rightarrow \frac{dp}{dT} = \left(\frac{s^\beta - s^\alpha}{v^\beta - v^\alpha} \right) = \frac{T(s^\beta - s^\alpha)}{T(v^\beta - v^\alpha)} = \frac{\lambda_{\beta\alpha}}{T(v^\beta - v^\alpha)} \quad \text{— 克拉珀龙方程}$$

$\lambda_{\beta\alpha}$: $\beta \rightarrow \alpha$ 的相变潜热

一级相变: μ 连续, μ' 不连续

ag 相变潜热随温度的变化

$$\begin{aligned} \frac{d\lambda}{dT} &= \frac{d(h^\beta - h^\alpha)}{dT} = \left(\frac{\partial h^\beta}{\partial T}\right)_p + \left(\frac{\partial h^\beta}{\partial p}\right)_T \frac{dp}{dT} - \left(\frac{\partial h^\alpha}{\partial T}\right)_p - \left(\frac{\partial h^\alpha}{\partial p}\right)_T \frac{dp}{dT} \\ &= C_p^\beta - C_p^\alpha + \left[\left(\frac{\partial h^\beta}{\partial p}\right)_T - \left(\frac{\partial h^\alpha}{\partial p}\right)_T \right] \frac{dp}{dT} \end{aligned}$$

$$\text{又有 } \left(\frac{\partial h}{\partial p}\right)_T = v - T \left(\frac{\partial v}{\partial T}\right)_p$$

$$\text{故 } \frac{d\lambda}{dT} = C_p^\beta - C_p^\alpha + \frac{\lambda}{T} - \left[\left(\frac{\partial v}{\partial T}\right)_p^\beta - \left(\frac{\partial v}{\partial T}\right)_p^\alpha \right] \frac{\lambda}{v^\beta - v^\alpha}$$

考虑气 \rightarrow 液相变, 认为 ideal gas, 则 $\frac{d\lambda}{dT} \approx C_p^\beta - C_p^\alpha$

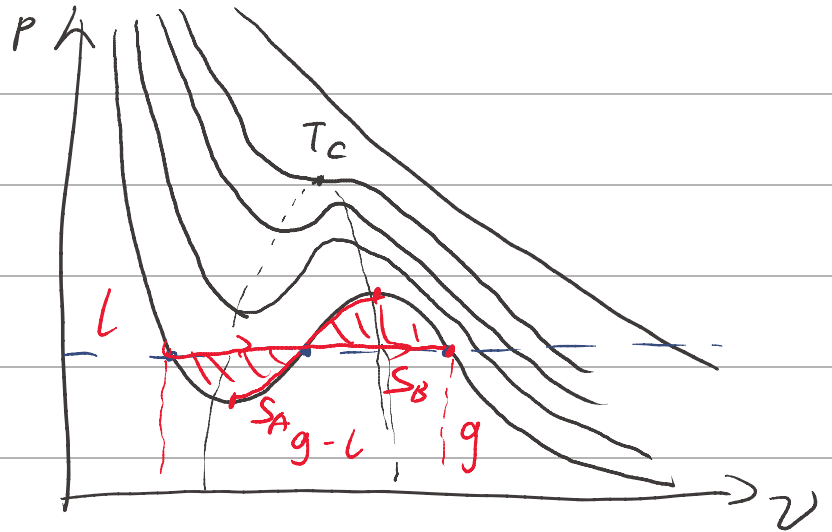
$v d w g$ 气液相变.

$$(p + \frac{a}{v^2})(v - b) = RT$$

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

$T > T_c$, 有一个实根.

$T < T_c$, 有三个实根.



相变位置: Maxwell 等面积法则

red: $(\frac{\partial p}{\partial v}) > 0$, 不满足稳定条件 ($K_T \geq 0$)

$$p = p_0 \text{ s.t. } S_A = S_B.$$

in reality, 相变会长至, \searrow 行为不会发生.

以临界点处的 p_c, v_c, T_c 为基准构造方程

$$\bar{p} = \frac{p}{p_c}, \quad \bar{v} = \frac{v}{v_c}, \quad \bar{t} = \frac{t}{t_c}$$

$$d\mu = -s dT + v dp$$

Landau = 二级相变理论.

关联长度 ξ 是源自临界区域或内体内部

$$\epsilon \sim |t|^{-\nu} \quad m \sim (-t)^{\beta}$$

序参量涨落之间的 Correlation function 的特性. T_c 附近, 涨落位于原点的序

$$C_V \sim |t|^{-\alpha} \quad m \sim |t|^{1/8}$$

$$\chi \sim |t|^{-\gamma}$$

序参量 $\delta m(0)$ 与 $\delta m(x)$ 的 CF 定义为 $C(x) = \langle \delta m(x) \delta m(0) \rangle$
 当 $|x| \rightarrow \infty$, $C(x) \rightarrow 0$, 临界行为 $C(x) \sim \frac{e^{-|x|/\xi}}{|x|^{d-2+\eta}}$
 第六个临界指数 η .

基本假设

① 序参量 m

- $m \neq 0$ 低温
- $m = 0$ 高温

② $f(m) = f_0 + \frac{a}{2} m^2 + \frac{b}{4} m^4 + \dots$

对称性自发破缺.

② 系统状态在 $f(m)$ 极小值给出.

e.g. 顺磁. 铁磁相变.

$$m \sim M(T, H)$$

$$f(m) = f_0 - mH + \frac{a(T)}{2} m^2 + \frac{b(T)}{4} m^4.$$

$$\frac{\partial f}{\partial m} = 0 \Rightarrow 0 = -H + am + bm^3.$$

1/2 临界点附近 ($T < T_c$):

$$m \sim \frac{H}{T - T_c}$$

$$\beta = \frac{1}{2}, \alpha = 0, \gamma = 1.$$

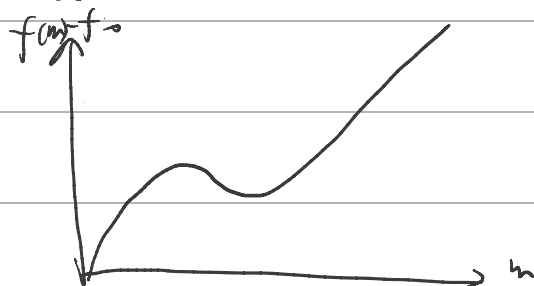
临界点. $a = 0$.

$$m^3 \sim H \quad \gamma = 3.$$

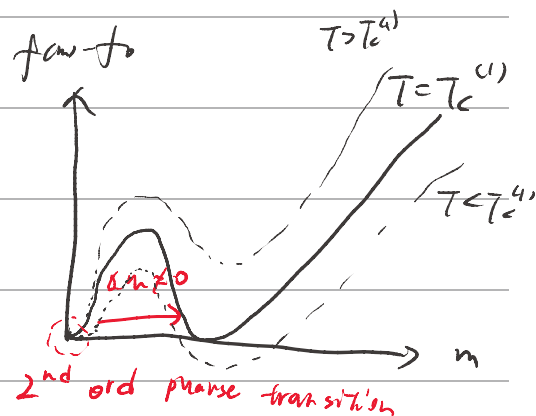
Landau - 一级相变理论

$$f(m) = f_0 + \frac{a(T)}{2} m^2 + \frac{b(T)}{4} m^4 + \frac{c(T)}{6} m^6 + \dots$$

设 $b(T) < 0$, $c(T) > 0$, $a(T) > 0$.



合适的参量



平衡状态 $T = T_c^{(1)}$:

$$\left\{ \begin{aligned} \frac{\partial f}{\partial m} \Big|_{m=m_0} &= a m_0 + b m_0^3 + c m_0^5 = 0 \\ f &= \frac{a}{2} m_0^2 + \frac{b}{4} m_0^4 + \frac{c}{6} m_0^6 = 0 \end{aligned} \right.$$

$$\Rightarrow m_0^2 = - \frac{3b(T_c^{(1)})}{4c(T_c^{(1)})} > 0.$$

$$a(T) = \frac{3b^2(T_c^{(1)})}{16c(T_c^{(1)})}$$

- 一级相变与宇宙学: 正物质与反物质的不对称 \Rightarrow 一级相变解释.

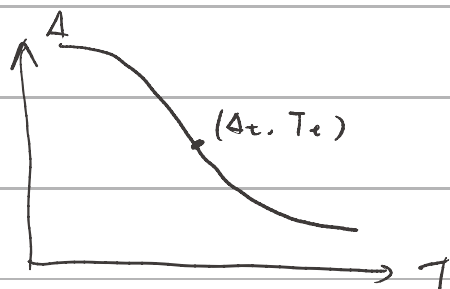
tricritical point \equiv 临界点

- 一级相变: $a = -\frac{3b^2}{16c}$ simultaneously? $a = b = 0$.

- 二级相变 $a = 0$.

若 $a = a(\Delta, T)$, $b = b(\Delta, T)$, $c = c(\Delta, T)$ Δ : 另一独立于 T 的参量.

求解 $a(\Delta, T) = b(\Delta, T) = 0 \Rightarrow \Delta = \Delta_c, T = T_c$.



曲线在交点处连续且导数亦连续.

$$\left. \frac{d\Delta}{dT} \right|_{(2)} = - \frac{\partial a / \partial T}{\partial a / \partial \Delta} = - \frac{a_T}{a_\Delta}$$

$$\left. \frac{d\Delta}{dT} \right|_{(1)} = - \frac{a_T c + c_T a - \frac{3}{8} b b_T}{a_\Delta c + c_\Delta a - \frac{3}{8} b b_\Delta}$$

$$\left. \frac{d\Delta}{dT} \right|_{(1)} = \left. \frac{d\Delta}{dT} \right|_{(2)}$$

研究 $\vec{x} = \begin{pmatrix} (T-T_c)/T_c \\ (\Delta-\Delta_c)/\Delta_c \end{pmatrix}$ 在 $\vec{x} \rightarrow 0$ 时的系统特性。

设 $a(\vec{x}) = \vec{a} \cdot \vec{x}$ ($\vec{x}=0$ 附近近似为线性)。

$$b(\vec{x}) = \vec{b} \cdot \vec{x}$$

$$\left. \frac{\partial f}{\partial m} \right|_t = (\vec{a} \cdot \vec{x}) m t (\vec{b} \cdot \vec{x})^2 + c m^5 = 0 \quad (m \neq 0)$$

$$\Rightarrow \textcircled{1} \vec{a} \perp \vec{x} \rightarrow m^2 \sim \vec{x} \rightarrow m \sim |\vec{x}|^{\frac{1}{2}}, \quad \beta = \frac{1}{2}$$

$$\Rightarrow \textcircled{2} \vec{b} \perp \vec{x} \rightarrow m^4 \sim \vec{x} \rightarrow m \sim |\vec{x}|^{\frac{1}{4}}, \quad t = \frac{1}{4}$$

连续相变的标度理论.

$\alpha, \beta, \gamma, \delta, \nu, \eta$.

标度假设 $f_s(t, h) \sim t^{2-\alpha} g_f(\frac{h}{t^\Delta})$ 描述 free energy 发散行为

$$t = \frac{T - T_c}{T_c}, h \sim H$$

内能发散行为 $U_s \sim \frac{\partial f}{\partial t} \sim (2-\alpha)t^{1-\alpha} g_f(h/t^\Delta) - \Delta h t^{1-\alpha-\Delta} g'_f(h/t^\Delta)$

$$\sim t^{1-\alpha} [(2-\alpha)g_f(h/t^\Delta) - \Delta \frac{h}{t^\Delta} g'_f(h/t^\Delta)]$$

$$\text{令 } x = h/t^\Delta \sim \tau$$

$$U_s \sim t^{1-\alpha} [(2-\alpha)g_f(x) - \Delta x g'_f(x)]$$

热容发散

$$C_s = -\frac{\partial^2 f}{\partial t^2} \sim t^{-\alpha} g_c(x)$$

$\Rightarrow \alpha$ 描述热容发散行为的临界指数.

磁化强度

$$m = \frac{\partial f}{\partial h} \sim t^{2-\alpha-\Delta} g_m(\frac{h}{t^\Delta})$$

$$\beta = 2 - \alpha - \Delta \Rightarrow \Delta = 2 - (\alpha + \beta)$$

假设 $g_m(x)$ 在 $x \rightarrow \infty$ 时 $\sim x^p$, 则

$$m(t \sim 0, h) \sim t^{2-\alpha-\Delta} \left(\frac{h}{t^\Delta}\right)^p.$$

$$\Rightarrow 2 - \alpha - \Delta = \Delta p, m \sim h^p \sim h^{\frac{1}{\delta}}$$

$$\Rightarrow \delta = \frac{1}{p} = \frac{\Delta}{2 - \alpha - \Delta} = \frac{\Delta}{\beta}$$

$$\gamma = 2\Delta - 2 + \alpha.$$

$$\Rightarrow \begin{cases} \alpha + 2\beta + \gamma = 1 & \textcircled{1} \text{ Rushbrooke 关系} \\ \delta - 1 = \frac{\gamma}{\beta} & \textcircled{2} \text{ Widom 关系} \end{cases}$$

关联长度. 关联函数

$$\xi(t, h) \sim t^{-2} g_{\xi}\left(\frac{h}{t^{\Delta}}\right)$$

$$\xi(t, 0) \sim t^{-2}, \text{ 设 } g_{\xi} \sim x^p \text{ 当 } x \rightarrow \infty, \text{ 则}$$

$$\xi(t \rightarrow 0, h) \sim t^{-2} \left(\frac{h}{t^{\Delta}}\right)^p = t^{-2-p\Delta} h^p.$$

关联长度按磁场强度的发育行为 $\xi \sim h^{-2\eta}$, $2\eta = -p = \frac{2}{\Delta}$.

超标度假设

$$\text{总自由能 } F(t, h) = \left(\frac{L}{\xi}\right)^d g_1(t, h) + \left(\frac{L}{a}\right)^d g_2(t, h).$$

L 为体系总尺度, a 为晶格常数, d 为体系的维度

热力学极限 $\left(\frac{L}{a}\right)^d \rightarrow \infty$ 时, $L \gg \xi \gg a$, 则

单位体积 F 发散部分 $f_s \sim \frac{F}{L^d} \sim t^{d\omega} g_f(x)$.

对比 $f_s \sim t^{2-\alpha} g_f(x)$ 得

$d\omega = 2 - \alpha$ Josephson 关系

$$\text{关联函数 } C(\vec{x}, t \rightarrow \infty, h) \sim \frac{1}{|\vec{x}|^{d-2+\eta}}$$

$$\text{铁磁相变 } \chi \sim \int d^d \vec{x} C(\vec{x}; t \rightarrow \infty, h) \sim \int \frac{\xi^d d^d \vec{x}}{|\vec{x}|^{d-2+\eta}} \sim \xi^{2-\eta} \sim t^{-2(2-\eta)} \sim t^{-\gamma}$$

$$\Rightarrow \gamma = 2(2-\eta) \quad \text{Fisher 关系}$$

~~Landau 相变理论~~ 满足一般假设下的标度关系, 但不满足基于超标度假设的 Josephson 与 Fisher 关系

explanation? — Statistical Physics.

CH4 多元系的相与化学平衡

对于多元系,

$$V = V(T, p, n_1, n_2, \dots, n_k)$$

$$U = U(T, p, n_1, n_2, \dots, n_k)$$

$$S = S(T, p, n_1, n_2, \dots, n_k)$$

由广延量的性质,

$$V(T, p, \lambda n_1, \lambda n_2, \dots, \lambda n_k) = \lambda V(T, p, n_1, n_2, \dots, n_k)$$

$$\Rightarrow \frac{\partial V}{\partial \lambda} = \sum_{i=1}^k n_i \left(\frac{\partial V}{\partial n_i} \right)_{T, p, n_{j \neq i}} = V$$

$$\text{故 } V = \sum_{i=1}^k n_i \left(\frac{\partial V}{\partial n_i} \right)_{T, p, n_j}$$

$$U = \sum_{i=1}^k n_i \left(\frac{\partial U}{\partial n_i} \right)_{T, p, n_j}$$

$$S = \sum_{i=1}^k n_i \left(\frac{\partial S}{\partial n_i} \right)_{T, p, n_j}$$

于是可以定义各自的偏摩尔量:

$$v_i = \left(\frac{\partial V}{\partial n_i} \right)_{T, p, n_j}$$

$$u_i = \left(\frac{\partial U}{\partial n_i} \right)_{T, p, n_j}$$

$$s_i = \left(\frac{\partial S}{\partial n_i} \right)_{T, p, n_j}$$

同理, 对 Gibbs 自由能, 也有

$$G = \sum_{i=1}^k n_i \mu_i$$

式中 $\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_j}$ 为第 i 个组元的化学势.

我们只考虑 $dG = -SdT + Vdp + \sum_{i=1}^k \mu_i dn_i$

$$\text{又: } dG = d\left(\sum_{i=1}^k \mu_i dn_i\right) = \sum_{i=1}^k (\mu_i dn_i + n_i d\mu_i)$$

$$\therefore SdT - Vdp + \sum_{i=1}^k n_i d\mu_i = 0 \quad \text{— Gibbs-Duhem 关系.}$$

三个强度量不再独立.

多元系的复相平衡与相律(无化学反应).

假设每一组元有两个可能的相 α 与 β ,且组元之间不进行化学反应.

$$\text{物质守恒: } \delta n_i^\alpha + \delta n_i^\beta = 0.$$

$$\text{显然, } \delta G = \sum_{i=1}^k (\mu_i^\alpha - \mu_i^\beta) \delta n_i^\alpha$$

$$\text{平衡条件: } \delta G = 0, \text{ 故 } \mu_i^\alpha = \mu_i^\beta \quad (i=1, 2, \dots, k)$$

设多元复相系有 k 个无化学反应的组元,每个组元有 ϕ 个相

$$\text{引入各相中的相对浓度 } x_i^\alpha = n_i^\alpha / n^\alpha, \quad n^\alpha = \sum_{i=1}^k n_i^\alpha.$$

$$\text{则有归一化条件 } \sum_{i=1}^k x_i^\alpha = 1. \quad (\text{约束} + \phi) \Rightarrow \text{每一相由 } T^\alpha, p^\alpha, n_1^\alpha, n_2^\alpha, \dots, n_{k-1}^\alpha$$

在达到平衡时,有热平衡

共 $k+1$ 个变量决定,共 $\phi(k+1)$ 个变量.

$$T^1 = T^2 = \dots = T^\phi \quad (\text{约束} + (\phi-1))$$

力学平衡

$$p^1 = p^2 = \dots = p^\phi \quad (\text{约束} + (\phi-1))$$

相平衡

$$\mu_i^1 = \mu_i^2 = \dots = \mu_i^\phi \quad (\text{约束} + k(\phi-1)).$$

故约束共 $(k+2)(\phi-1)$ 个.

$$\text{故系统自由度为 } \phi(k+1) - (k+2)(\phi-1) = k - \phi + 2.$$

自由度不得小于0, 故 $k - \phi + 2 \geq 0$

因此, 单相系最多三相平衡.

Chemical reaction.

任意化学反应, 可将生成物与反应物列同一边, 写做

$$\sum_{i=1}^K \nu_i A_i = 0.$$

规定生成物的系数为正, 反应物的系数为负.

Dalton定律: $\Delta n_i = \nu_i \Delta n$.

Δn 为多元共同的摩尔比例系数.

讨论等温等压条件下的 CR.

$$\Delta Q = T \Delta S$$

定义定压反应热为

$$Q_p = \Delta H = \sum_{i=1}^K \nu_i h_i.$$

$$\text{则 } \left(\frac{\partial \Delta H}{\partial T} \right)_p = \sum_{i=1}^K \nu_i C_{p,i}$$

在等温等压条件下, 化学平衡时, $\delta G = 0$.

$$\delta G = \sum \mu_i \delta n_i = \delta n \sum \nu_i \mu_i = 0$$

故有 $\sum \nu_i \mu_i = 0$, 此即化学平衡条件.

若不平衡, 则反应向 $\Delta G < 0$ 的方向进行.

$$\because \Delta G = \Delta n \sum \nu_i \mu_i$$

\therefore 当 $\sum \nu_i \mu_i < 0$, $\Delta n > 0$, 反应正向进行.

当 $\sum \nu_i \mu_i > 0$, $\Delta n < 0$, 反应逆向进行.

混合理想气体

$$P = \sum_{i=1}^K p_i$$

$$\text{where } p_i = n_i \frac{RT}{V} \Rightarrow PV = (n_1 + n_2 + \dots + n_K) RT.$$

计算混合理想气体的 U 与 S .

对于混合气体中的第 i 个组分, 其化学势

$$\mu_i(T, p) = RT [\phi_i(T) + \ln(p_i)] = RT [\phi_i(T) + \ln(x_i p)].$$

$$\text{where } \phi_i(T) = - \int \frac{dT}{RT^2} \int C_{p,i}(T) dT + \frac{h_{0,i}}{RT} - \frac{S_{0,i}}{R}.$$

于是体系的 Gibbs 自由能为

$$G = \sum_{i=1}^K \mu_i n_i = \sum_{i=1}^K n_i RT [\phi_i(T) + \ln(x_i p)].$$

$$\text{由 differential equation, 有 } V = \left(\frac{\partial G}{\partial p} \right)_{T, n_i} = \frac{\sum_{i=1}^K n_i RT}{p} \quad (\text{分压定律}).$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_{p, n_i} = \sum_{i=1}^K n_i R [\phi_i(T) + T \phi_i'(T)]$$

$$= \sum_{i=1}^K n_i \left[\int C_{p,i} \frac{dT}{T} - R \ln x_i p + S_{0,i} \right]$$

$$= \sum_{i=1}^K n_i \left[\int C_{p,i} \frac{dT}{T} - R \ln p + S_{0,i} \right] - \sum_{i=1}^K n_i R \ln x_i$$

$$= \sum_{i=1}^K n_i S_i - \underbrace{\sum_{i=1}^K n_i R \ln x_i}_{\text{气体混合熵变}}.$$

若存在化学反应,

气体混合熵变.

$$\text{定义平衡常数 } K_p(T): \ln K_p(T) = - \sum_i \nu_i \phi_i(T).$$

$$\text{平衡条件: } \sum_i \nu_i \mu_i = 0 \Rightarrow \sum_i \nu_i [\phi_i(T) + \ln p_i]$$

$$\text{则有 } \ln K_p(T) = \sum_i \nu_i \ln p_i.$$

$$\Rightarrow K_p(T) = \prod_i p_i^{\nu_i}$$

$$\text{若考虑 } K(T, p), \text{ 则代入 } p_i = x_i p: K(T, p) = p^{-\sum_i \nu_i} \cdot K_p(T).$$

$$\text{范托夫方程: } \frac{d}{dT} \ln K_p(T) = \frac{\Delta H}{RT^2}$$

理想溶液.

溶液中有组元 n_1, n_2, \dots, n_k , 不失一般性, 定义 n_1 为溶剂且 $n_1 \gg n_2$.
记稀溶液的内能为 U , 则 稀溶液

$$\frac{U}{n_1} = u_1(T, p) + \sum_{i=2}^k \frac{\partial U}{\partial n_i} \frac{n_i}{n_1} = u_1(T, p) + \sum_{i=2}^k u_i(T, p) \frac{n_i}{n_1} + \dots$$

取稀溶液近似, 则有

$$U = \sum_{i=1}^k u_i(T, p) n_i.$$

$$\text{同理, } V = \sum_{i=1}^k v_i(T, p) n_i.$$

系统的熵:

$$\begin{aligned} TdS &= dU + pdV = \sum_{i=1}^k n_i du_i + p \sum_{i=1}^k n_i dv_i \\ &= \sum_{i=1}^k n_i (du_i + p dv_i) \end{aligned}$$

注意到 $du_i + p dv_i$ 有 entropy 的微分的形式, 故有

$$S = \sum_{i=1}^k n_i s_i^*(T, p) + C, \quad T s_i^* = du_i + p dv_i.$$

C 的确定: 当稀溶液连续接近理想气体, S 趋于混合理想气体具有相同的形式.

$$\text{故 } C \text{ 即 } G \text{ 的混合熵: } C = -R \sum_{i=1}^k n_i \ln x_i.$$

$$\text{于是 } S = \sum_{i=1}^k n_i (s_i^* - R \ln x_i)$$

$$\text{立刻得到 } G = U - TS + PV = \sum_{i=1}^k n_i u_i - n_i T (s_i^* - R \ln x_i) + p v_i n_i.$$

$$= \sum_{i=1}^k n_i (u_i - T s_i^* + p v_i) + \sum_{i=1}^k n_i R \ln x_i$$

$$= \sum_{i=1}^k n_i g_i + \sum_{i=1}^k n_i R \ln x_i$$

于是 $\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_j} = g_i + R \ln x_i$ 若溶液的化学势由该式给出, 则称作理想溶液.

对于非理想溶液, 定义活度: $a_i = \gamma_i x_i$ 来代替原来的 x_i .

γ_i 称为组元 i 的活度系数.

$$\text{则 } \mu_i = g_i + RT [\ln x_i + \ln \gamma_i].$$

再将平方场理论计算强电解质溶液的活度系数.

考虑理想溶液与某个组元的蒸气达到平衡的问题.

$$\text{由平衡条件, } \mu_i^g(T, p) = \mu_i^l(T, p).$$

$$\text{故 } g_i + RT \ln x_i = RT [\phi_i(T) + \ln p_i].$$

$$\Rightarrow \text{于是 } \ln p_i = \ln x_i + \frac{g_i}{RT} - \phi_i(T)$$

$$p_i = k_i x_i \text{ where } k_i = \exp \left[\frac{g_i}{RT} - \phi_i(T) \right].$$

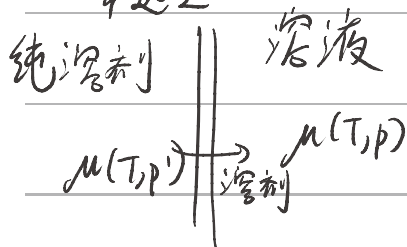
这就是 Henry 定律: 一定温度与压强下, 溶质蒸气分压与其在溶液中的相对浓度成正比.

$$\text{拉乌尔定律: } \frac{p_i^0 - p_i}{p_i^0} = \sum_{i \neq 1} x_i$$

where p_i^0 为纯溶剂在温度为 T 、压强为 p 时溶剂的饱和压

渗透压.

可以证明, 半透膜两边溶液中溶剂的化学势相等



$$\mu(T, p') = g(T, p') + RT \ln x_1 = \mu(T, p)$$

对溶剂的化学势作 Taylor 展开, 则

$$\mu(T, p') - \mu(T, p) \approx \frac{\partial \mu}{\partial p} (p' - p) = \frac{\partial \mu}{\partial p} \Pi$$

$$\text{又: 纯溶液中 } g(T, p') = \mu(T, p')$$

$$\Rightarrow -RT \ln x_1 = \Pi v' \quad \text{where } v' = \frac{\partial \mu}{\partial p}. \quad \text{又: } x_1 + \sum_{i=1}^k x_i = 1, \quad \sum_{i=1}^k x_i \ll 1$$

两边同乘溶剂物质的量, 得

$$\therefore \Pi v' = RT \sum_{i=1}^k x_i$$

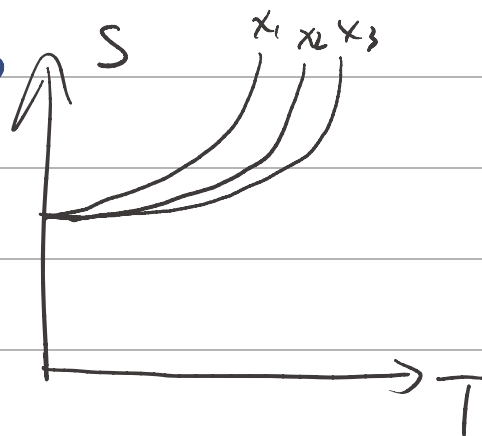
$$\Pi V = \sum_{i=1}^k n_i RT \Rightarrow \Pi = \sum_{i=1}^k c_i RT \Rightarrow \text{范托夫渗透压方程}$$

3rd Law of Thermodynamics.

Nernst: $\Delta S(T) \equiv \int_{x_1}^{x_2} \frac{\partial Q}{T} \bigg|_T = S(x_2, T) - S(x_1, T)$

1906

$\lim_{T \rightarrow 0} \Delta S(T) = 0$. "0th": $\lim_{N \rightarrow \infty} \frac{\ln g(N)}{N} = 0$



More ambitious version.

$\lim_{T \rightarrow 0} S(x, T) = 0$, for all x .

Consequences:

①. $S(x, T) - S(x, 0) = \int_0^T \frac{dQ}{T} = \int_0^T \frac{C(T')}{T'} dT'$

in order to keep $S(x, 0)$ reserved, $C(T) \rightarrow 0$ as $T \rightarrow 0$

more precisely, $[C_x(T) \sim T^n]$ $n \geq 1$.

showing quantum behavior.

$S(0) = k \ln g$

ground state degeneracy

② Expansivity.

$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = - \frac{1}{V} \left(\frac{\partial S}{\partial P} \right)_T \xrightarrow{T \rightarrow 0} 0$

note that $C_p - C_v = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \xrightarrow{T \rightarrow 0} 0$

therefore $\lim_{T \rightarrow 0} C_p = \lim_{T \rightarrow 0} C_v$