1. 表面系统

p	V	T
$-\sigma$	A	T

$$đW = p\,dV$$

$$đW = -\sigma\, dA$$

<u>粒子数不守恒</u>

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$p \to -\sigma$, $V \to A$ $\Rightarrow \left(\frac{\partial U}{\partial A}\right)_T = -T\frac{d\sigma}{dT} + \sigma$ 仅含T

$$\Rightarrow \boxed{U = A\left[-T\frac{d\sigma}{dT} + \sigma\right]} + \cancel{f(T)}^{\,0}$$

$$dU = \boxed{\sigma\, dA} + \cancel{A\, d\sigma} - \left[T\frac{d\sigma}{dT}dA + \cancel{A\frac{d\sigma}{dT}dT} + AT\,d\left(\frac{d\sigma}{dT}\right)\right]$$

$$= T\,dS + \sigma\, dA$$

$$\Rightarrow dS = -\left[dA\frac{d\sigma}{dT} + A\,d\left(\frac{d\sigma}{dT}\right)\right] = -d\left(A\frac{d\sigma}{dT}\right)$$

$$\Rightarrow S = -A\frac{d\sigma}{dT} + \cancel{C}_{\,0}$$

$$\begin{cases} U = A\left(\sigma - T\frac{d\sigma}{dT}\right) \\ S = -A\frac{d\sigma}{dT} \end{cases}$$

$\Rightarrow$ 自由能 $F = U - TS = A\sigma$

Gibbs 自由能 $G = F + pV \to F - \sigma A = 0$

2. 热力学函数

第一次习题课中 广延量、强度量

$dU = TdS - pdV \qquad U(S, V)$

粒子数不守恒系统

$dU = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \frac{\partial U}{\partial n} dn \qquad U(S, V, n)$

$T \qquad -p \qquad \mu$

$dU = TdS - pdV + \mu dn$

$U((1+\varepsilon)S, (1+\varepsilon)V, (1+\varepsilon)n) = (1+\varepsilon) U$

$\|$

$U + \frac{\partial U}{\partial S} \varepsilon S + \frac{\partial U}{\partial V} \varepsilon V + \frac{\partial U}{\partial n} \varepsilon n$ (T, p, μ 不变)

$\Rightarrow \boxed{U = \frac{\partial U}{\partial S} S + \frac{\partial U}{\partial V} V + \frac{\partial U}{\partial n} n = TS - pV + \mu n}$

齐次函数
欧拉定理

自由能 $F = U - TS$

$dF = -SdT - pdV + \mu dn$

$F(T, V, n)$

焓 $H = U + pV$

$dH = TdS + Vdp + \mu dn$

$H(S, p, n)$

可以证明 广延 $F(x_1 \cdots x_n, y)$ 强 广

$\|$

$f(x_1 \cdots x_n)\, y$

强

Gibbs 自由能 $G = U + pV - TS$

$dG = -SdT + Vdp + \mu dn$

$G(T, p, n) = g(T, p)\, n$

强 广

代入欧拉方程：$G = (TS - pV + \mu n) + pV - TS = \mu n$

$\therefore \mu = \mu(T, p)$

$\mu = \frac{G}{n}$ 广 广 强

$nd\mu + \mu dn = -SdT + Vdp + \mu dn$

$\Rightarrow d\mu = -\frac{S}{n} dT + \frac{V}{n} dp = -s dT + v dp$

复平衡条件：　　单元二相情况

孤立系统 熵判据 $dS=0$

$$\begin{cases} \text{总内能 } dU = T_1 dS_1 - p_1 dV_1 + \mu_1 dn_1 + T_2 dS_2 - p_2 dV_2 + \mu_2 dn_2 = 0 \\ \text{总粒子 } dn = dn_1 + dn_2 = 0 \end{cases}$$

$\Rightarrow$

$T_1 = T_2$　热平衡

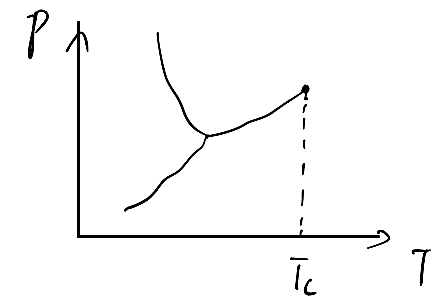
$p_1 = p_2$　力学平衡

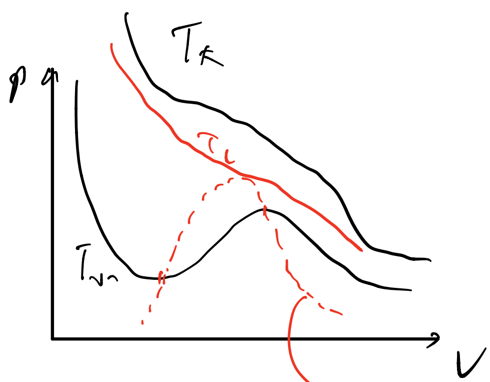
$\mu_1 = \mu_2$　相平衡

$$\mu_1 = \mu_2 \Rightarrow d\mu_1 = d\mu_2 \Rightarrow -s_1 dT + v_1 dp = -s_2 dT + v_2 dp$$

$$\Rightarrow \frac{dp}{dT} = \frac{s_1 - s_2}{v_1 - v_2} = \frac{L}{T(v_1 - v_2)}$$　克拉珀龙方程

临界点





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

$$dp(V-b) - dV\left(\frac{2a}{V^3}(V-b) - \left(p + \frac{a}{V^2}\right)\right) = 0$$

$$\frac{dp}{dV} = 0 \Rightarrow \frac{2a}{V^3} - \frac{1}{V-b}\left(p + \frac{a}{V^2}\right) = 0 \Rightarrow \boxed{p = \frac{a}{v^2} - \frac{2ab}{v^3}}$$

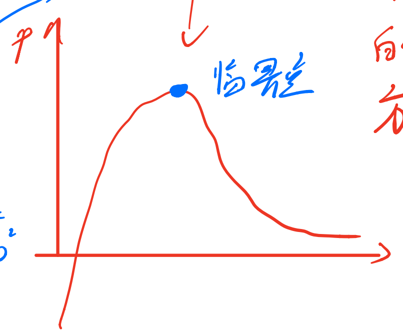
范德瓦耳斯气体满足 $\frac{dp}{dV}=0$ 的点组成的方程

求这个的

$$\frac{dp}{dV} = 0 \Rightarrow -\frac{2a}{v^3} + \frac{6ab}{v^4} = 0 \Rightarrow V_c = 3b$$

代回

得 $p_c = \frac{a}{27b^2}$



代回状态方程 $\Rightarrow T_c = \frac{8a}{27bR}$