第三章

单元系的相变

§3.1 热动平衡判据

为了判定在给定的外加约束条件下系统的某些状态是否为稳定的平衡状态，设想系统围绕该状态发生各种可能的自发虚变动。

1、基本平衡判据

熵判据　　孤立系统：$dS \geq \dfrac{dQ}{T} \Rightarrow dS \geq 0$

孤立系统的熵永不减少，在平衡态达到极大值

$\Delta S = 0$　中性平衡

$\Delta S < 0$　稳定平衡

熵判据：系统(孤立系统)处在稳定平衡状态的充要条件为

$$\Delta S < 0$$

ΔS可以围绕极值点做泰勒展开。

$$\Delta S \equiv \delta S + \frac{1}{2!}\delta^2 S$$

熵在 x_0 取极大值要求：$\delta S = 0$ $\delta^2 S < 0$

$\delta S = 0$ 给出平衡条件，

$\delta^2 S < 0$ 给出平衡的稳定性条件。

1）、等温等容系统---自由能判据

平衡态是熵最大的态 $\Longrightarrow$ 平衡态自由能最小

$F = U - TS \Longrightarrow \Delta F > 0$

平衡条件： $\delta F = 0$

稳定平衡： $\delta^2 F > 0$

2）、等温等压系统---吉布斯判据

平衡态是熵最大的态。 $\Longrightarrow$ 平衡态吉布斯函数最小

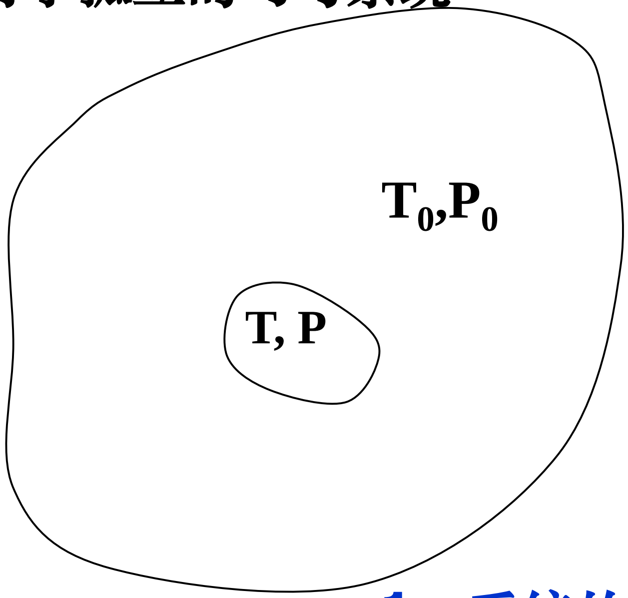
$G = U - TS + PV \Longrightarrow \Delta G > 0$

平衡条件： $\delta G = 0$

稳定平衡： $\delta^2 G > 0$

三、均匀系统热动平衡条件

对于孤立的均匀系统



系统的体积V不变，内能U不变。

子系统虚变动和系统其余部分虚变动满足：

$$\delta U_0 + \delta U = 0,$$

$$\delta V_0 + \delta V = 0$$

系统总熵变 $\Delta \tilde{S} = \Delta S_0 + \Delta S \approx \delta \tilde{S} + \frac{1}{2}\delta^2 \tilde{S}$

$$\Delta S_0 \approx \delta S_0 + \frac{1}{2}\delta^2 S_0 \qquad \Delta S \approx \delta S + \frac{1}{2}\delta^2 S$$

$\Delta \tilde{S} < 0$ 平衡稳定条件

1、系统的平衡条件： $\delta \tilde{S} = \delta S + \delta S_0 = 0$

根据 $\delta S = \frac{\delta U + p\delta V}{T}$ $\qquad \delta S_0 = \frac{\delta U_0 + p_0 \delta V_0}{T_0} = -\frac{\delta U + p_0 \delta V}{T_0}$

代入平衡条件得到： $\delta S = \delta U (\frac{1}{T} - \frac{1}{T_0}) + \delta V (\frac{p}{T} - \frac{p_0}{T_0}) = 0$

上页得到： $\delta S=\delta U(\frac{1}{T}-\frac{1}{T_0})+\delta V(\frac{p}{T}-\frac{p_0}{T_0})=0$

由于虚变动δU、δV可任意变化，故上式要求：

$$T=T_0 \qquad p=p_0$$

结果表明：达到平衡时整个系统的温度和压强是均匀的！

2、稳定平衡 $\delta^2\tilde{S}=\delta^2 S_0+\delta^2 S<0$

$$\delta^2 S=\frac{\partial^2 S}{\partial U^2}(\delta U)^2+2\frac{\partial^2 S}{\partial U\partial V}\delta U\delta V+\frac{\partial^2 S}{\partial V^2}(\delta V)^2<0$$

$$\delta^2 S_0=\frac{\partial^2 S_0}{\partial U_0^2}(\delta U_0)^2+2\frac{\partial^2 S_0}{\partial U_0\partial V_0}\delta U_0\delta V_0+\frac{\partial^2 S_0}{\partial V_0^2}(\delta V_0)^2.$$

$s\sim s_0, u\sim u_0, v\sim v_0$, where $S=ns$.

$$\frac{\partial^2 S}{\partial U^2}=\frac{1}{n}\frac{\partial^2 s}{\partial u^2},\ (\delta U=-\delta U_0,\ \delta V=-\delta V_0.)$$

近似有 $\delta^2\tilde{S}\approx\delta^2 S<0$ $\qquad |\delta^2 S_0|<<|\delta^2 S|$

$$\delta^2 \tilde{S} \simeq \delta^2 S = \frac{\partial^2 S}{\partial U^2}(\delta U)^2 + 2\frac{\partial^2 S}{\partial U \partial V}\delta U \delta V + \frac{\partial^2 S}{\partial V^2}(\delta V)^2.$$
$$= \left[\frac{\partial}{\partial U}\frac{\partial S}{\partial U}\delta U + \frac{\partial}{\partial V}\frac{\partial S}{\partial U}\delta V\right]\delta U$$
$$+ \left[\frac{\partial}{\partial U}\frac{\partial S}{\partial V}\delta U + \frac{\partial}{\partial V}\frac{\partial S}{\partial V}\delta V\right]\delta V,$$

$dU = T\mathrm{d}S - p\mathrm{d}V$ $\quad \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}, \left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T}.$

$$\delta^2 S = \left[\frac{\partial}{\partial U}\left(\frac{1}{T}\right)\delta U + \frac{\partial}{\partial V}\left(\frac{1}{T}\right)\delta V\right]\delta U$$
$$+ \left[\frac{\partial}{\partial U}\left(\frac{p}{T}\right)\delta U + \frac{\partial}{\partial V}\left(\frac{p}{T}\right)\delta V\right]\delta V$$
$$= \delta\left(\frac{1}{T}\right)\delta U + \delta\left(\frac{p}{T}\right)\delta V.$$

以T,V为自变量 $\quad U = U(T, V)$

$$\delta U = \left(\frac{\partial U}{\partial T}\right)_V \delta T + \left(\frac{\partial U}{\partial V}\right)_T \delta V$$
$$= C_V \delta T + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\delta V.$$

$$\delta^2 S = \delta\left(\frac{1}{T}\right)\delta U + \delta\left(\frac{p}{T}\right)\delta V.$$

$$\delta U = C_V \delta T + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\delta V.$$

$$\delta\frac{1}{T} = \left(\frac{\partial}{\partial T}\frac{1}{T}\right)_V \delta T + \left(\frac{\partial}{\partial V}\frac{1}{T}\right)_T \delta V = -\frac{1}{T^2}\delta T.$$

$$\begin{aligned}
\delta\frac{p}{T} &= \left(\frac{\partial}{\partial T}\frac{p}{T}\right)_V \delta T + \left(\frac{\partial}{\partial V}\frac{p}{T}\right)_T \delta V \\
&= \left[p\left(\frac{\partial}{\partial T}\frac{1}{T}\right)_V + \frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_V\right]\delta T \\
&\quad + \left[p\left(\frac{\partial}{\partial V}\frac{1}{T}\right)_T + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_T\right]\delta V \\
&= \left[-\frac{p}{T^2} + \frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_V\right]\delta T + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_T \delta V \\
&= \frac{1}{T^2}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\delta T + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_T \delta V.
\end{aligned}$$

$$\delta^2 S = \delta\left(\frac{1}{T}\right)\delta U + \delta\left(\frac{p}{T}\right)\delta V.$$

$$\delta^2\tilde{S} \simeq \delta^2 S = -\frac{1}{T^2}\delta T\left\{C_V\delta T + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\delta V\right\}$$
$$+\left\{\frac{1}{T^2}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\delta T + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_T\delta V\right\}\delta V$$

$$\delta^2 S = -\frac{C_V}{T^2}(\delta T)^2 + \frac{1}{T}\frac{\partial p}{\partial V}\Big|_T(\delta V)^2] < 0$$

V,T 相互独立，T>0，故要求：

$$C_V > 0 \qquad \frac{\partial p}{\partial V}\Big|_T < 0$$

平衡稳定性条件

讨论:

1、**子系统温度略高于媒质：**由平衡条件，子系统传递热量而使温度降低，于是子系统恢复平衡

2、子系统体积收缩：由平衡条件，子系统的压强将增加，于是子系统膨胀而恢复平衡

习题 (3.4)

$$\delta^2 S < 0 \Rightarrow \begin{cases} C_V > 0, \\ \left(\dfrac{\partial p}{\partial V}\right)_T < 0 \end{cases} \qquad \begin{matrix} \Rightarrow C_p > 0, \\ \Rightarrow \left(\dfrac{\partial p}{\partial V}\right)_S < 0 \end{matrix}$$

证明:

$$\left.\begin{matrix} C_V > 0, \\ C_p - C_V = -T\dfrac{\left(\dfrac{\partial p}{\partial T}\right)_V^2}{\left(\dfrac{\partial p}{\partial V}\right)_T} = \dfrac{VT\alpha^2}{\kappa_T} > 0, \end{matrix}\right\} \quad C_p \geq C_V > 0,$$

$$\left.\begin{matrix} \left(\dfrac{\partial p}{\partial V}\right)_T < 0 \\ \dfrac{\kappa_S}{\kappa_T} = \dfrac{-\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_S}{-\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_T} = \dfrac{C_V}{C_p} \leq 1 \end{matrix}\right\} \quad \left(\dfrac{\partial p}{\partial V}\right)_S \leq \left(\dfrac{\partial p}{\partial V}\right)_T < 0,$$

§ 3. 2 开系的热力学基本方程

一、基本概念

单元系:化学上纯的物质系统,只含一种化学组分(一个组元).

复相系:一个系统不是均匀的,但可以分为若干个均匀的部分.

水和水蒸气共存---单元两相系;冰,水和水蒸气共存---单元三相系

二、化学势 μ

在复相系中,由于不同系之间存在转换,故每一个相的摩尔数是变化的,即为开系.

对于闭系： $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$

对于开系： $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu dn$

$$\boxed{\mu = \left(\frac{\partial G}{\partial n}\right)_{T,\ p}}$$ —— 化学势

G是广延量，系统的吉布斯函数与其摩尔数成正比

$$G(T,p,n)=nG_m(T,p)$$

$$\mu=\frac{\partial G}{\partial n}\Big|_{T,p}=G_m(T,p)$$

$$\boxed{\mathrm{d}G=-S\mathrm{d}T+V\mathrm{d}p+\mu dn}$$

已知特性函数G(T,p,n),可求得：$S=-\left(\frac{\partial G}{\partial T}\right)_{p,n},\ V=\left(\frac{\partial G}{\partial p}\right)_{T,n},\ \mu=\left(\frac{\partial G}{\partial n}\right)_{T,p}$

$$G=U-TS+pV=\mu n,$$

$$U=G+TS-pV \Rightarrow \begin{cases} U=-pV+TS+\mu n, \\ \boxed{dU=TdS-pdV+\mu dn} \end{cases} \qquad \mu=\left(\frac{\partial U}{\partial n}\right)_{S,V}$$

$$dU=-pdV-Vdp+TdS+SdT+\mu dn+nd\mu,$$

吉布斯关系

$$\boxed{-Vdp+SdT+nd\mu=0,}$$

$$\boxed{d\mu=\frac{V}{n}dp-\frac{S}{n}dT,}$$

$$H=G+TS=U+pV \Rightarrow \begin{cases} H=U+pV=TS+\mu n, \\ \boxed{dH=TdS+Vdp+\mu dn} \end{cases} \qquad \mu=\left(\frac{\partial H}{\partial n}\right)_{S,p}$$

$$F=G-pV=U-TS \Rightarrow \begin{cases} F=U-TS=-pV+\mu n, \\ \boxed{dF=-SdT-pdV+\mu dn} \end{cases} \qquad \mu=\left(\frac{\partial F}{\partial n}\right)_{T,V}$$

$$dU = TdS - pdV + \mu dn, \quad \Rightarrow \quad \mu = \left(\frac{\partial U}{\partial n}\right)_{S,V}, \quad T = \left(\frac{\partial U}{\partial S}\right)_{n,V}, \quad p = -\left(\frac{\partial U}{\partial V}\right)_{n,S},$$

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_{S,n} = -\left(\frac{\partial p}{\partial S}\right)_{V,n},} \quad \boxed{\left(\frac{\partial T}{\partial n}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{n,V},} \quad \boxed{\left(\frac{\partial \mu}{\partial V}\right)_{S,n} = -\left(\frac{\partial p}{\partial n}\right)_{S,V},}$$

麦克斯韦关系

$$dH = TdS + Vdp + \mu dn, \quad \Rightarrow \quad \mu = \left(\frac{\partial H}{\partial n}\right)_{S,p},$$

$$\boxed{\left(\frac{\partial T}{\partial p}\right)_{S,n} = \left(\frac{\partial V}{\partial S}\right)_{p,n},} \quad \boxed{\left(\frac{\partial T}{\partial n}\right)_{S,p} = \left(\frac{\partial \mu}{\partial S}\right)_{n,p},} \quad \boxed{\left(\frac{\partial \mu}{\partial p}\right)_{S,n} = \left(\frac{\partial V}{\partial n}\right)_{S,p},}$$

麦克斯韦关系

$$dF = -SdT - pdV + \mu dn, \quad \Rightarrow \quad \mu = \left(\frac{\partial F}{\partial n}\right)_{T,V},$$

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial p}{\partial T}\right)_{V,n},} \quad \boxed{\left(\frac{\partial S}{\partial n}\right)_{T,n} = -\left(\frac{\partial \mu}{\partial T}\right)_{n,V},} \quad \boxed{\left(\frac{\partial \mu}{\partial V}\right)_{T,n} = -\left(\frac{\partial p}{\partial n}\right)_{T,V},}$$

麦克斯韦关系

$$dG = -SdT + Vdp + \mu dn, \quad \Rightarrow \quad \mu = \left(\frac{\partial G}{\partial n}\right)_{T,p},$$

$$\boxed{\left(\frac{\partial S}{\partial p}\right)_{T,n} = -\left(\frac{\partial V}{\partial T}\right)_{p,n},} \quad \boxed{\left(\frac{\partial S}{\partial n}\right)_{T,p} = -\left(\frac{\partial \mu}{\partial T}\right)_{n,p},} \quad \boxed{\left(\frac{\partial \mu}{\partial p}\right)_{T,n} = \left(\frac{\partial V}{\partial n}\right)_{T,p},}$$

麦克斯韦关系

定义:巨热力势

$$J = F - \mu n$$

$$\boxed{dF = -SdT - pdV + \mu dn}$$

全微分:

$$dJ = -SdT - pdV - nd\mu$$

***J*是以*T*, *V*, *μ*为独立变量的特性函数**

$$S = -\left(\frac{\partial J}{\partial T}\right)_{V,\mu},\ p = -\left(\frac{\partial J}{\partial V}\right)_{T,\mu},\ n = -\left(\frac{\partial J}{\partial \mu}\right)_{T,V}$$

巨热力势J也可表为:

$$J = F - G = -pV$$

$$G = nG_m = n\mu$$

习题:

3.7.证明: $\left(\frac{\partial U}{\partial n}\right)_{T,V} - \mu = -T\left(\frac{\partial \mu}{\partial T}\right)_{V,n}$,

(1) $$\left(\frac{\partial U}{\partial n}\right)_{T,V} = \left(\frac{\partial (F+TS)}{\partial n}\right)_{T,V} = \left(\frac{\partial F}{\partial n}\right)_{T,V} + T\left(\frac{\partial S}{\partial n}\right)_{T,V} = \mu - T\left(\frac{\partial \mu}{\partial n}\right)_{n,V}$$

(2) $$dU = TdS - pdV + \mu dn = T\left(\left(\frac{\partial S}{\partial T}\right)_{V,n} dT + \left(\frac{\partial S}{\partial V}\right)_{T,n} dV \boxed{+\left(\frac{\partial S}{\partial n}\right)_{T,V} dn}\right) - pdV \boxed{+\mu dn} =,$$

2. 证明: $\mu = \left(\frac{\partial U}{\partial n}\right)_{T,p} + p\left(\frac{\partial \mu}{\partial p}\right)_{T,n} + T\left(\frac{\partial \mu}{\partial p}\right)_{T,n}$,

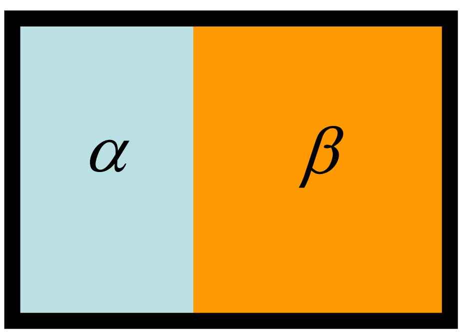
(1) $$\left(\frac{\partial U}{\partial n}\right)_{T,p} = \left(\frac{\partial (G+TS-pV)}{\partial n}\right)_{T,p} = \left(\frac{\partial G}{\partial n}\right)_{T,p} + T\left(\frac{\partial S}{\partial n}\right)_{T,p} - p\left(\frac{\partial V}{\partial n}\right)_{T,p} = \mu - T\left(\frac{\partial \mu}{\partial T}\right)_{n,p} - p\left(\frac{\partial \mu}{\partial p}\right)_{n,T},$$

(2) $$dU = TdS - pdV + \mu dn = \ldots dT + \ldots dp + \ldots dn,$$

§3.3 单元系的复相平衡条件

一、平衡条件

以单元二相系为例,由α，β表示两个相,构成一个孤立系:（U^{α}，V^{α}，n^{α}，T^{α}）（U^{β}，V^{β}，n^{β}，T^{β}）



孤立系统

无能量交换： $U^{\alpha}+U^{\beta}=const$

无相互作用： $V^{\alpha}+V^{\beta}=const$

无物质交换： $n^{\alpha}+n^{\beta}=const$

则有：

$$\delta U^{\alpha}+\delta U^{\beta}=0$$

$$\delta V^{\alpha}+\delta V^{\beta}=0$$

$$\delta n^{\alpha}+\delta n^{\beta}=0$$

又开系的热力学基本方程：

$$dU = TdS - pdV + \mu dn$$

对每一个相，熵变：

$$\delta S^{\alpha} = \frac{\delta U^{\alpha} + p^{\alpha}\delta V^{\alpha} - \mu^{\alpha}\delta n^{\alpha}}{T^{\alpha}}, \quad \delta S^{\beta} = \frac{\delta U^{\beta} + p^{\beta}\delta V^{\beta} - \mu^{\beta}\delta n^{\beta}}{T^{\beta}}$$

整个系统的熵变为：

$$\delta S = \delta S^{\alpha} + \delta S^{\beta}$$

$$= \delta U^{\alpha}\left(\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}}\right) + \delta V^{\alpha}\left(\frac{p^{\alpha}}{T^{\alpha}} - \frac{p^{\beta}}{T^{\beta}}\right) - \delta n^{\alpha}\left(\frac{\mu^{\alpha}}{T^{\alpha}} - \frac{\mu^{\beta}}{T^{\beta}}\right)$$

当复相系统平衡时,总熵满足极大值, 故恒有$\delta S=0$.

考虑到变动过程中，δU^{α} ,δV^{α} ,δn^{α}为相互独立的变量：

$T^{\alpha} = T^{\beta}$（热平衡），$p^{\alpha} = p^{\beta}$（力学平衡），$\mu^{\alpha} = \mu^{\beta}$（相变平衡）

讨论：如果上述平衡条件未能满足，复相系将发生变化，变化进行的方向如何？

1. 仅热平衡条件不满足：

$$\therefore \delta S = \delta U^{\alpha}\left(\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}}\right) + \delta V^{\alpha}\left(\frac{p^{\alpha}}{T^{\alpha}} - \frac{p^{\beta}}{T^{\beta}}\right) - \delta n^{\alpha}\left(\frac{\mu^{\alpha}}{T^{\alpha}} - \frac{\mu^{\beta}}{T^{\beta}}\right) > 0$$

$$\delta U^{\alpha}\left(\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}}\right) > 0$$

若$T^{\alpha} > T^{\beta}$,则$\delta U^{\alpha} < 0$ 即能量将从高温α相传到低温β相去。

2. 仅力学平衡条件不满足：

$$\therefore \delta S = \delta U^{\alpha}\left(\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}}\right) + \delta V^{\alpha}\left(\frac{p^{\alpha}}{T^{\alpha}} - \frac{p^{\beta}}{T^{\beta}}\right) - \delta n^{\alpha}\left(\frac{\mu^{\alpha}}{T^{\alpha}} - \frac{\mu^{\beta}}{T^{\beta}}\right) > 0$$

$$\delta V^{\alpha}\left(\frac{p^{\alpha}}{T^{\alpha}} - \frac{p^{\beta}}{T^{\beta}}\right) > 0$$

若$p^{\alpha} > p^{\beta}$,则$\delta V^{\alpha} > 0$

即压强大的相将膨胀，压强小的相将被压缩。

3. 仅相平衡条件不满足：

$$\therefore \delta S = \delta U^{\alpha}\left(\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}}\right) + \delta V^{\alpha}\left(\frac{p^{\alpha}}{T^{\alpha}} - \frac{p^{\beta}}{T^{\beta}}\right) - \delta n^{\alpha}\left(\frac{\mu^{\alpha}}{T^{\alpha}} - \frac{\mu^{\beta}}{T^{\beta}}\right) > 0$$

$$-\delta n^{\alpha}\left(\frac{\mu^{\alpha}}{T^{\alpha}} - \frac{\mu^{\beta}}{T^{\beta}}\right) > 0$$

若$\mu^{\alpha} > \mu^{\beta}$,则$\delta n^{\alpha} < 0$

即物质将由化学势高的相转移到化学势低的相去。

$$dS = \frac{\mathrm{d}U + pdV - \mu dn}{T}$$

$$\delta^2 S < 0 \qquad C_V > 0 \qquad \frac{\partial p}{\partial V}\Big|_{T,\ u} < 0 \qquad \frac{\partial u}{\partial n}\Big|_{T,\ V} > 0$$

§3.4 单元复相系的平衡性质

单元系的相图

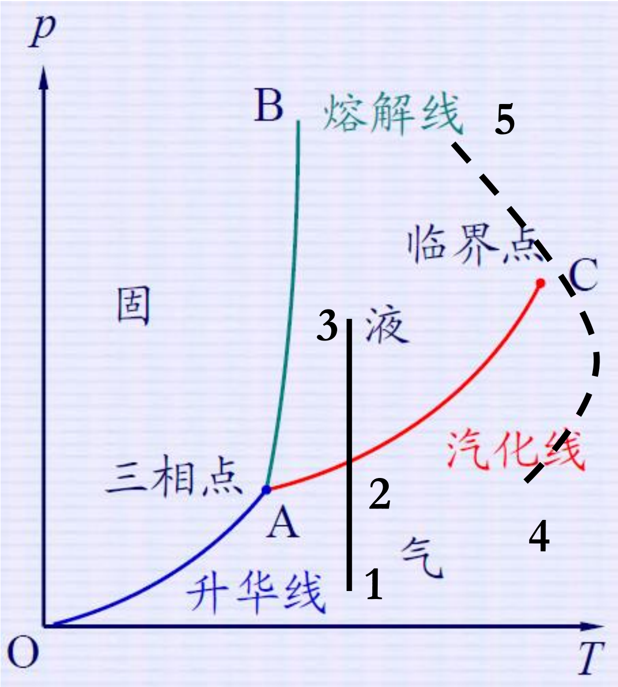
AC: 汽化曲线；

AB: 熔解曲线；

AO: 升华曲线。

A： 三相点

C: 临界点。



相变潜热

水三相点：T=273.16K，P=610.9Pa。

单元系三相共存：

$$\begin{cases} T^{\alpha}=T^{\beta}=T^{\gamma}=T \\ p^{\alpha}=p^{\beta}=p^{\gamma}=p \\ \mu^{\alpha}(T,p)=\mu^{\beta}(T,p)=\mu^{\gamma}(T,p) \end{cases}$$

***T*、*p*完全确定，不再独立改变**

两相平衡

以单元两相系为例， ***α*，*β***

$$T^{\alpha}=T^{\beta}=\mathrm{T}$$

$$p^{\alpha}=p^{\beta}=\mathrm{p}$$

$$\mu^{\alpha}(T,p)=\mu^{\beta}(T,p)$$

两相平衡曲线上只有一个参量是独立的

利用相平衡性质，导出克拉珀龙方程

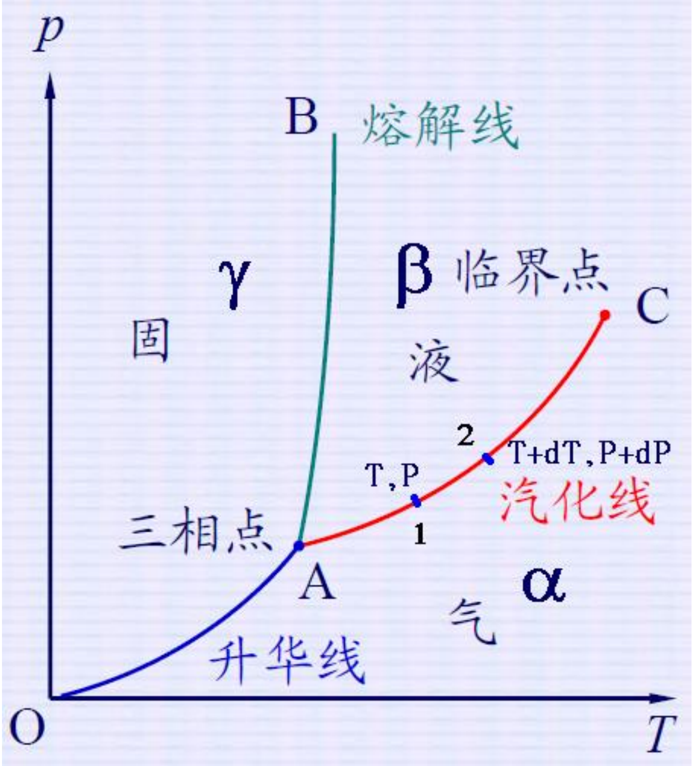
考虑相平衡性质，相平衡曲线上有

平衡曲线上有相邻两点：

$$A(T,p),B(T+dT,p+dp)$$

有 $\mu^{\alpha}(T,p)=\mu^{\beta}(T,p)$

$$\mu^{\alpha}(T+dT,p+dp)=\mu^{\beta}(T+dT,p+dp)$$



$$d\mu^{\alpha}=\mu^{\alpha}(T+dT,p+dp)-\mu^{\alpha}(T,p)$$

$$d\mu^{\beta}=\mu^{\beta}(T+dT,p+dp)-\mu^{\beta}(T,p)$$

$$\therefore d\mu^{\alpha}=d\mu^{\beta}$$

1mol物质的G就是化学势 μ：

$$d\mu = dG_m = -S_m dT + V_m dp.$$

$$d\mu^\alpha = d\mu^\beta$$

$$-S_m^\alpha dT + V_m^\alpha dp = -S_m^\beta dT + V_m^\beta dp.$$

$$\frac{dp}{dT} = \frac{S_m^\beta - S_m^\alpha}{V_m^\beta - V_m^\alpha},$$

$$\mathrm{d}S = \text{đ}Q/T \Rightarrow \Delta Q = T\Delta S.$$

定义潜热 $L = T(S_m^\beta - S_m^\alpha)$,

$$\boxed{\frac{dp}{dT} = \frac{L}{T(V_m^\beta - V_m^\alpha)}.}$$

克拉珀龙方程

三、 蒸气压方程

饱和蒸气: 与凝聚相(液相或固相)达到平衡的蒸气.

蒸气压方程: 描述饱和蒸气压与温度的关系的方程.

α **: 凝聚相** β **:气相**

$$\boldsymbol{V_m^{\alpha} \ll V_m^{\beta}} \qquad pV_m^{\beta} = RT$$

$$\boxed{\frac{dp}{dT} = \frac{L}{T(V_m^{\beta} - V_m^{\alpha})}.}$$

$$\frac{1}{p}\frac{dp}{dT} = \frac{L}{RT^2}$$

相变潜热方程: 习题 (3.13)

$$\mu^\alpha = \mu^\beta \rightarrow h^\alpha - Ts^\alpha = h^\beta - Ts^\beta$$

$$L = T(s^\beta - s^\alpha)$$

$$\Rightarrow \quad L = h^\beta - h^\alpha$$

$$\Rightarrow \quad \frac{dL}{dT} = \frac{dh^\beta}{dT} - \frac{dh^\alpha}{dT}$$

$$dh^\alpha = c_p^\alpha dT + \left[\upsilon^\alpha - T\left(\frac{\partial \upsilon^\alpha}{\partial T}\right)_p \right] dp,$$

$$dh^\beta = c_p^\beta dT + \left[\upsilon^\beta - T\left(\frac{\partial \upsilon^\beta}{\partial T}\right)_p \right] dp,$$

$$\Rightarrow \quad \frac{dL}{dT} = c_p^\beta - c_p^\alpha + \left[\upsilon^\beta - \upsilon^\alpha + T\left(\frac{\partial \upsilon^\alpha}{\partial T}\right)_p - T\left(\frac{\partial \upsilon^\beta}{\partial T}\right)_p \right] \frac{dp}{dT},$$

$$\frac{dp}{dT} = \frac{L}{T(V_m^\beta - V_m^\alpha)}.$$

$$\frac{dL}{dT} = c_p^\beta - c_p^\alpha + \frac{L}{T} + \left[\left(\frac{\partial \upsilon^\alpha}{\partial T}\right)_p - \left(\frac{\partial \upsilon^\beta}{\partial T}\right)_p \right] \frac{L}{\upsilon^\beta - \upsilon^\alpha}$$

$$v^\beta \gg v^\alpha$$

（b为蒸汽相a是凝聚相）

$$\frac{dL}{dT} = c_p^\beta - c_p^\alpha$$

§ 3.5 临界点和气液两相的转变

实验结果:

1. 高于31.1℃, 等温线符合玻意耳定律PV=C

2.该等温线在温度31.1℃以下可分为三部分。

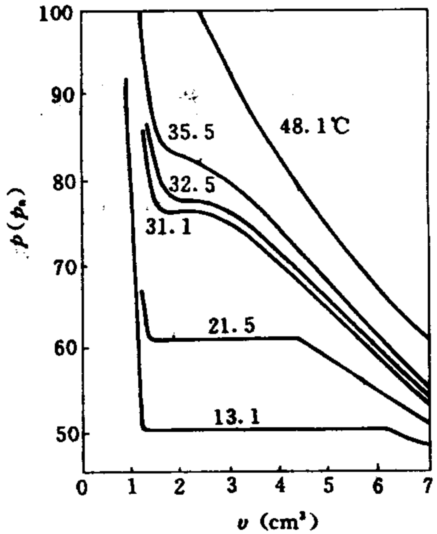
(*a*) 气态：C->B

(*b*)气液共存: A-B

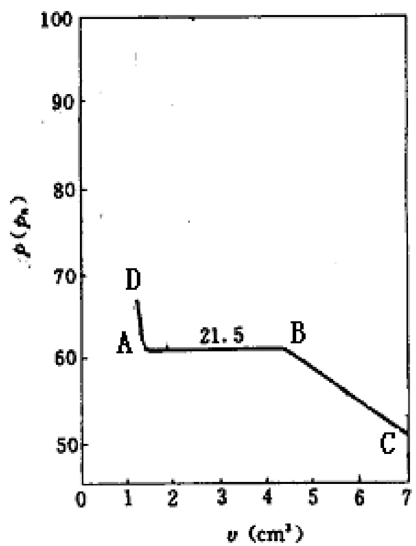
比体积: υ_g: 气态， υ_l: 液态

A-B: $\upsilon = x\upsilon_l + (1-x)\upsilon_g$ (*x* 液态所占比例)

(*c*)液态: A-D



安德鲁斯, 1869, CO_2等温线.



3.在温度31.1℃，液体和蒸汽没有分别。相应的温度为临界温度，相应的压强称为临界压强。

$$\left(\partial p/\partial V\right)_T = 0$$

§ 3. 7 相变的分类

相变:存在相变潜热，存在体积突变

一、分类

$$L = T(S_m^{\beta} - S_m^{\alpha}),$$

化学势连续　　**相平衡时**　　$$\boldsymbol{d\mu = -S_m dT + V_m dp}$$

$$\mu^{(1)}(T,p) = \mu^{(2)}(T,p)$$

一级相变:

$$\frac{\partial \mu^{(1)}}{\partial T} \neq \frac{\partial \mu^{(2)}}{\partial T}, \quad (s^{(1)} \neq s^{(2)}) \qquad \frac{\partial \mu^{(1)}}{\partial p} \neq \frac{\partial \mu^{(2)}}{\partial p}, (v^{(1)} \neq v^{(2)})$$

特点:

1.相变点为两相化学势的交点 ；2.两相可以共存;

3.一阶导数不连续，有相变潜热和体积突变;

4.存在亚稳态。

二级相变：

$$\frac{\partial \mu^{(1)}}{\partial T}=\frac{\partial \mu^{(2)}}{\partial T}, \quad \left(s^{(1)}=s^{(2)} \right) \qquad \frac{\partial \mu^{(1)}}{\partial p}=\frac{\partial \mu^{(2)}}{\partial p}, \left(v^{(1)}=v^{(2)} \right)$$

$$\frac{\partial^2 \mu^{(1)}}{\partial T^2}\neq\frac{\partial^2 \mu^{(2)}}{\partial T^2}, \qquad \frac{\partial^2 \mu^{(1)}}{\partial T \partial p}\neq\frac{\partial^2 \mu^{(2)}}{\partial T \partial p}, \qquad \frac{\partial^2 \mu^{(1)}}{\partial p^2}\neq\frac{\partial^2 \mu^{(2)}}{\partial p^2},$$

$$c_p=T\frac{\partial s}{\partial T}\bigg|_p=-T\frac{\partial^2 \mu}{\partial T^2}, \qquad \alpha=\frac{1}{v}\frac{\partial v}{\partial T}\bigg|_p=\frac{1}{v}\frac{\partial^2 \mu}{\partial T \partial p},$$

$$\kappa_T=-\frac{1}{v}\frac{\partial v}{\partial p}\bigg|_T=-\frac{1}{v}\frac{\partial^2 \mu}{\partial p^2},$$

均不连续。

等等，由此类推

二级及以上的相变－连续相变

艾伦菲斯特方程： 二级相变点压强随温度变化的斜率公式

$$\boxed{\frac{dp}{dT}=\frac{\alpha^{(2)}-\alpha^{(1)}}{\kappa_T^{(2)}-\kappa_T^{(1)}}.}\qquad \boxed{\frac{dp}{dT}=\frac{c_p^{(2)}-c_p^{(1)}}{Tv(\alpha^{(2)}-\alpha^{(1)})}.}$$

证： 由二级相变不存在相变潜热和体积突变，在邻近的相变点（**T,P**）和（**T+dT，P+dP**）两相的比熵和比体积变化相等，即

ds（1）= ds（2） 且 **s（1）= s（2）**

dv（1）= dv（2） **v（1）= v（2）**

又 $$dv=(\frac{\partial v}{\partial T})_P dT+(\frac{\partial v}{\partial P})_T dp=\alpha v dT-\kappa v dP$$

$$\Longrightarrow\quad \alpha^{(1)}v^{(1)}dT-\kappa^{(1)}v^{(1)}dP=\alpha^{(2)}v^{(2)}dT-\kappa^{(2)}v^{(2)}dP$$

$$\Longrightarrow\quad \alpha^{(1)}dT-\kappa^{(1)}dP=\alpha^{(2)}dT-\kappa^{(2)}dP\quad\Longrightarrow\quad \frac{dP}{dT}=\frac{\alpha^{(2)}-\alpha^{(1)}}{\kappa^{(2)}-\kappa^{(1)}}$$

同理
$$ds = (\frac{\partial s}{\partial T})_P dT + (\frac{\partial s}{\partial P})_T dp = \frac{c_p}{T} dT - (\frac{\partial v}{\partial T})_P dP$$

$$= \frac{c_p}{T} dT - avdP$$

麦氏关系

$$(\frac{\partial s}{\partial P})_T = -(\frac{\partial v}{\partial T})_P$$

$$\Longrightarrow \quad \frac{c_p{}^{(1)}}{T} dT - a^{(1)} v^{(1)} dP = \frac{c_p{}^{(2)}}{T} dT - a^{(2)} v^{(2)} dP$$

$$\Longrightarrow \quad \frac{dP}{dT} = \frac{c_p{}^{(2)} - c_p{}^{(1)}}{Tv(a^{(2)} - a^{(1)})}$$

作业：3.4，3.6，3.7， 3.13，3.18，3.19