§3.1 热动平衡判据

1. 熵判据

孤立系 $\mathrm{d}S \geq 0$

平衡态S极大。

对系统的状态虚变动，熵的虚变动ΔS

$$\Delta S < 0$$

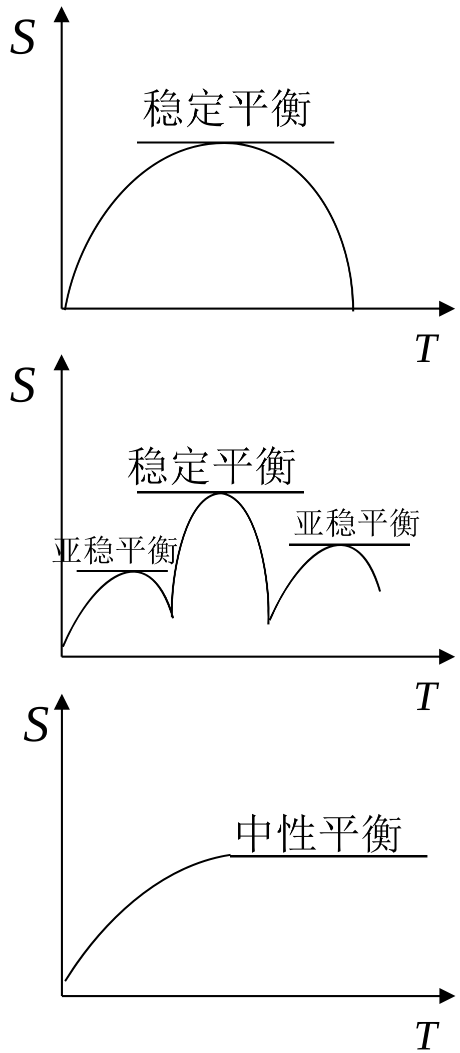
孤立系统处在稳定平衡状态的必要和充分条件为:

$$\Delta S < 0$$

将S泰勒展开，准确到二级。有

$$S = S_0 + \delta S + \frac{1}{2}\delta^2 S$$

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



平衡态的必要条件 $\delta S = 0$

$\delta^2 S < 0$　$\Delta S < 0$　极大值　稳定平衡

最大极值　稳定平衡

较小极值　亚稳平衡

$\Delta S = 0$　常数值　中性平衡

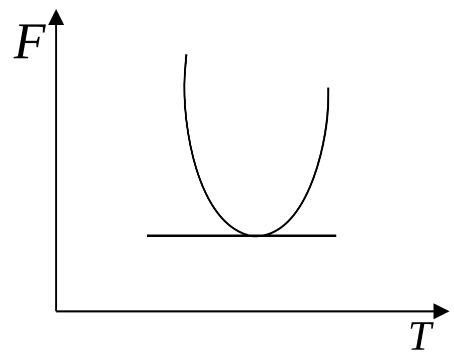
2. 等温等容系统 ——自由能判据

平衡态自由能最小　　$\Delta F > 0$

$$\Delta F = \delta F + \delta_2 F$$

平衡条件：　$\delta F = 0$

稳定平衡：　$\delta^2 F > 0$



等温等容系统处在稳定平衡状态的必要和充分条件为:

$$\Delta F > 0$$

3. 等温等压系统 ——吉布斯函数判据

平衡态吉布斯函数最小 $\Delta G > 0$

$$\Delta G = \delta G + \delta^2 G$$

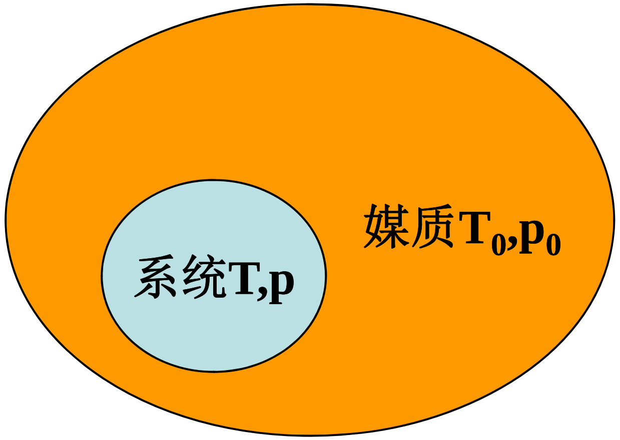
平衡条件： $\delta G = 0$

稳定平衡： $\delta^2 G > 0$

等温等压系统处在稳定平衡状态的必要和充分条件为：

$$\Delta G > 0$$

4. 孤立系统热动平衡条件和平衡稳定性条件



孤立大系统

媒质很大，有恒定的温度和压强。

整个系统的 V 不变，U不变。

子系统虚变动δU，δV

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

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

熵的广延性 $\Delta \tilde{S} = \Delta S + \Delta S_0$

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

$$\Delta S_0 = \delta S_0 + \frac{1}{2}\delta^2 S_0$$

孤立系统极值要求 $\delta \tilde{S} = \delta S + \delta S_0 = 0$

$$dU = TdS - pdV \quad \Rightarrow \quad \delta S = \frac{1}{T}\delta U + \frac{p}{T}\delta V$$

$$\delta\tilde{S} = \delta S + \delta S_0 = \delta U\left(\frac{1}{T} - \frac{1}{T_0}\right) + \delta V\left(\frac{p}{T} - \frac{p_0}{T_0}\right) = 0$$

系统处于平衡状态 $T = T_0, \quad p = p_0$ ——热动平衡条件

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

$$\delta^2 S_0 << \delta^2 S$$

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

$$S = S(U, V) \quad \delta S = \left(\frac{\partial S}{\partial U}\right)_V \delta U + \left(\frac{\partial S}{\partial V}\right)_U \delta V$$

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

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

$$= \delta U\left(\frac{\partial}{\partial U}\left(\frac{\partial S}{\partial U}\right)_V \delta U + \frac{\partial}{\partial V}\left(\frac{\partial S}{\partial U}\right)_V \delta V\right) + \delta V\left(\frac{\partial}{\partial U}\left(\frac{\partial S}{\partial V}\right)_U \delta U + \frac{\partial}{\partial V}\left(\frac{\partial S}{\partial V}\right)_U \delta V\right)$$

$$= \delta U \delta\left(\frac{\partial S}{\partial U}\right)_V + \delta V \delta\left(\frac{\partial S}{\partial V}\right)_U$$

$$dU = TdS - pdV \quad \Rightarrow \quad dS = \frac{1}{T}dU + \frac{p}{T}dV$$

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

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

$$= \frac{1}{T}\left[-\frac{\delta U + p\delta V}{T}\delta T + \delta p \delta V\right] = \frac{1}{T}\left[-\delta S \delta T + \delta p \delta V\right] < 0$$

以（T, V）为变量

$$\delta^2 S = \frac{1}{T}\left[-\delta S\delta T + \delta p\delta V\right]$$

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

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

$$= -\frac{C_V}{T^2}(\delta T)^2 + \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_T (\delta V)^2 < 0$$

平衡的稳定性条件： $C_V > 0, \quad \left(\frac{\partial p}{\partial V}\right)_T < 0$

§ 3.2 开系热力学基本方程

1. 单元复相系的特点

- 复相系中的任一相都是均匀的开系，由于有相变发生，因而一个相的质量或摩尔数不守恒；整个系统是闭系。
- 复相系中每一相的平衡态热力学性质都可用状态参量来描述。各相的状态参量不完全独立，互相联系。

2. 开系热力学基本方程

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu \mathrm{d}n \qquad G(T, p, n)$$

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p}$$ 叫系统的化学势。

单元单相 $\mu = G_\mathrm{m} = \frac{G}{n}$ $\qquad G(T,p,n) = nG_m(T,p) = n\mu$

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

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

$$G = U - TS + pV$$

$$U = G + TS - pV$$

$$dU = dG + TdS + SdT - pdV - Vdp$$

$$= -SdT + Vdp + \mu dn + TdS + SdT - pdV - Vdp$$

$$\boxed{dU = TdS - pdV + \mu dn} \qquad U = U(S, V, n)$$

$$H = G + TS = U + pV$$

$$\boxed{\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p + \mu\mathrm{d}n}$$

$$H = H(S, p, n)$$

$$F = G - pV = U - TS$$

$$\boxed{\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}n}$$

$$F = F(T, V, n)$$

3. 巨热力势

$$J = F - \mu n = F - G = -pV$$

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

$$\boxed{\mathrm{d}J = -S\mathrm{d}T - p\mathrm{d}V - n\mathrm{d}\mu}$$

$$J = J(T, V, \mu)$$

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

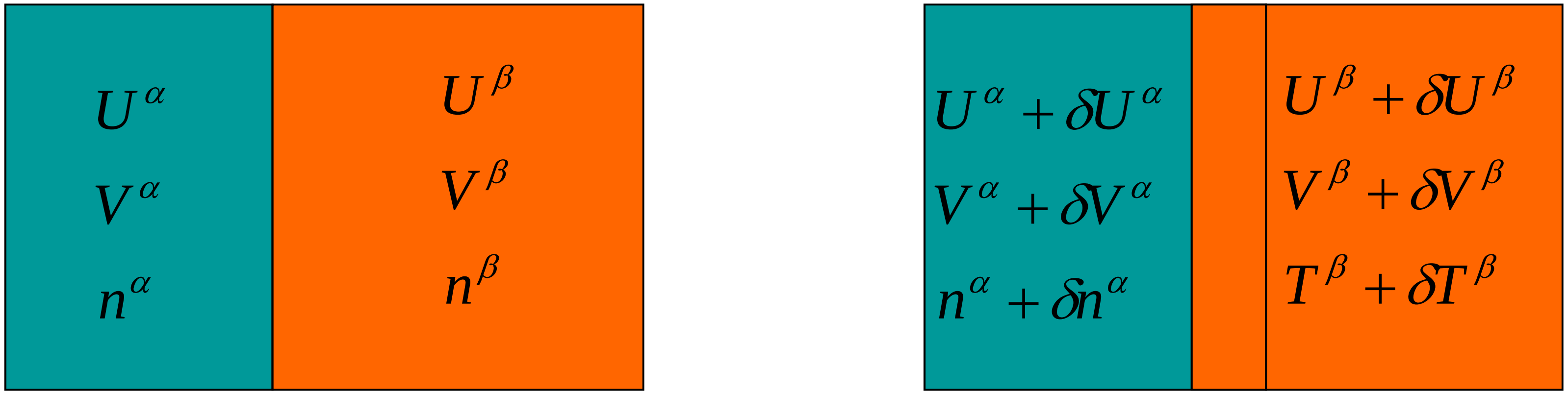
§ 3.3 单元系的复相平衡

1. 单元两相系

α、β两相（或两子系）⟶ 孤立系

$\delta S = 0$

平衡 ⟺ 平衡



$U^\alpha + U^\beta =$ 常量　　　$\delta U^\alpha + \delta U^\beta = 0$

$V^\alpha + V^\beta =$ 常量　　　$\delta V^\alpha + \delta V^\beta = 0$

$n^\alpha + n^\beta =$ 常量　　　$\delta n^\alpha + \delta n^\beta = 0$

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

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

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

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

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

2. 平衡条件

总熵极大值， $\delta S = 0$

$$\frac{1}{T^\alpha} - \frac{1}{T^\beta} = 0 \qquad \frac{p^\alpha}{T^\alpha} - \frac{p^\beta}{T^\beta} = 0 \qquad \frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta} = 0$$

热平衡条件 $T^\alpha = T^\beta$

→ 力平衡条件 $p^\alpha = p^\beta$

相平衡条件 $\mu^\alpha = \mu^\beta$

- 复相系的平衡条件：整个单元二相系达到平衡时，两相的温度，压强和化学势必须分别相等。

此结论对于三相，四相等复相系均适用。

讨论： 非平衡 $\xrightarrow[\delta S>0]{}$ 平衡

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

① 若热平衡条件不满足，即 $T^{\alpha}>T^{\beta},p^{\alpha}=p^{\beta},\mu^{\alpha}=\mu^{\beta}$

则 $\delta U_{\alpha}<0$ 即热量从高温(α)相传递到低温(β)相

② 若力学平衡条件不满足，即 $p^{\alpha}>p^{\beta},T^{\alpha}=T^{\beta},\mu^{\alpha}=\mu^{\beta}$

则 $\delta V_{\alpha}>0$ 压强大的相(α)将膨胀，压强小的相(β)将压缩。

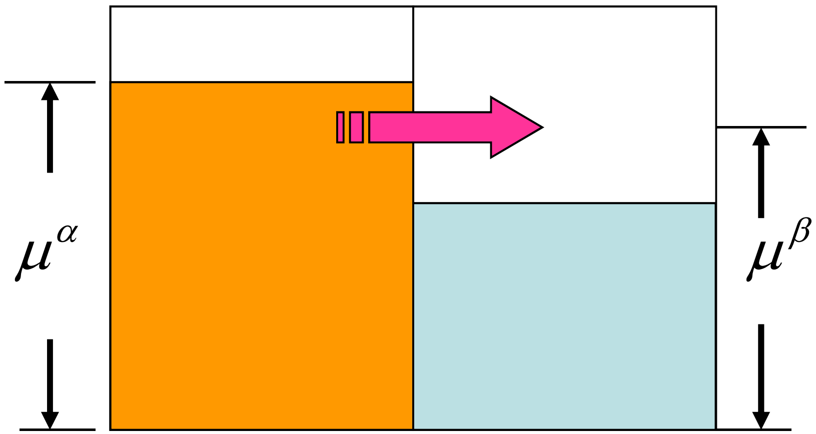
③ 若相变平衡条件不满足，即 $\mu^{\alpha}>\mu^{\beta},p^{\alpha}=p^{\beta},T^{\alpha}=T^{\beta}$

则 $\delta n_{\alpha}<0$ 物质由化学势高的相(α)转移到化学势低的相(β)

化学势

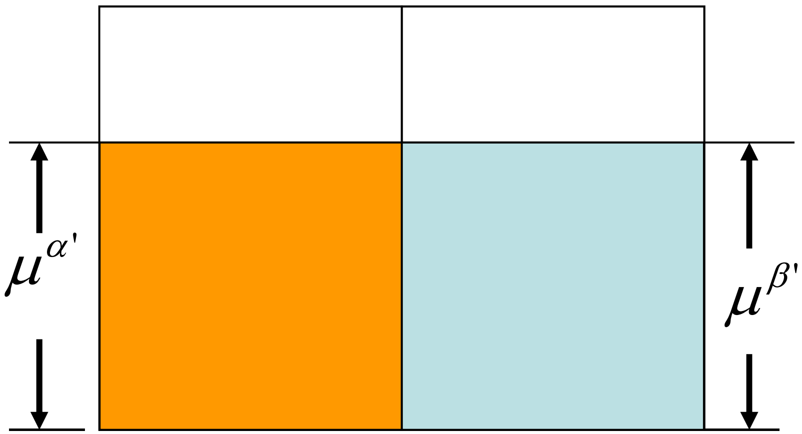
$$\mu^{\alpha} > \mu^{\beta} \Rightarrow \delta n^{\alpha} < 0$$ 粒子方向

粒子从化学势高的相向低的相跑！！



化学不平衡

$$\mu^{\alpha} > \mu^{\beta}$$



化学平衡

$$\mu^{\alpha'} = \mu^{\beta'}$$

化学势差促使粒子流动。

作业：P106:

3.1;　　3.2;　　3.3;　　3.4