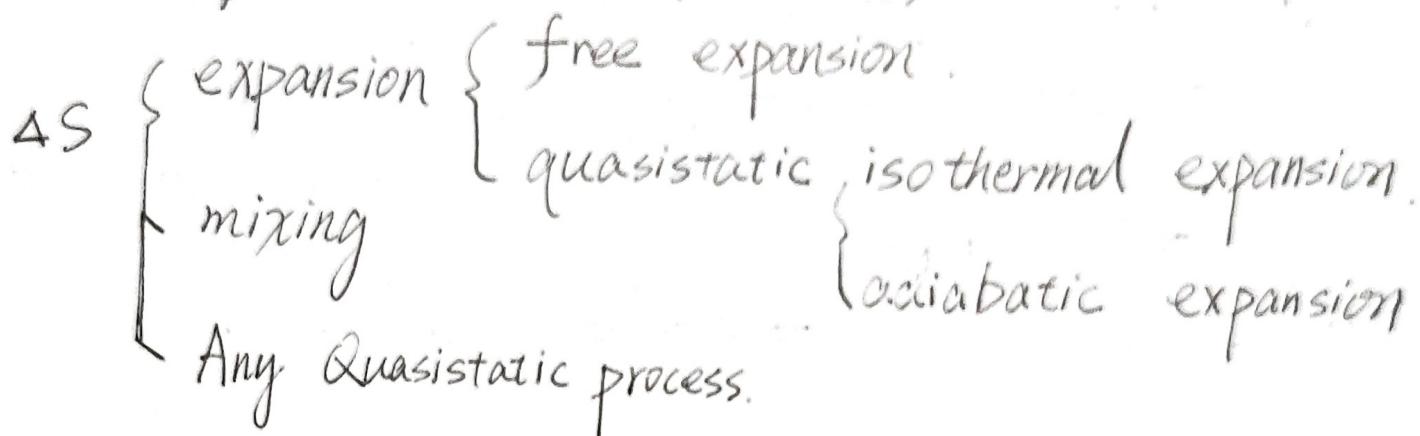


The Second Law of Thermodynamics.

"Entropy tends to increase."

$$S = k \ln \Omega \quad \text{for macrostate in equilibrium}$$

I. ΔS for some instances / Processes / Interactions.



1. free expansion.

$$S = Nk \ln V + \frac{3}{2} Nk \ln U + k \ln f(v)$$

$$\Delta N = 0 \quad \Delta U = W + Q = 0 + 0 = 0$$

$$\Delta S = S_f - S_i = Nk \ln \frac{V_f}{V_i}$$

2. quasistatic isothermal expansion.

$$\Delta N = 0 \quad \Delta U = W + Q = \frac{1}{2} Nk \Delta T = 0$$

$$\Delta S = S_f - S_i = Nk \ln \frac{V_f}{V_i}; Q = -W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} \frac{NkT}{V} dV$$

$$\Delta S = \frac{Q}{T} \quad \Leftrightarrow Q = NkT \ln \frac{V_f}{V_i} = T \Delta S$$

3. quasistatic adiabatic expansion.

$$\Delta S = \int_{V_i}^{V_f} dS = \int \frac{Q=0}{T} = 0. \quad \text{"isentropic"}$$

4. mixing. $\Delta N_A = 0$. $\Delta U_A = W + Q = 0$. $\Delta N_B = 0$. $\Delta U_B = 0$.

$$\Delta S = \Delta S_A + \Delta S_B = N_A k \ln \frac{V}{V_A} + N_B k \ln \frac{V}{V_B} = -Nk(x_A \ln x_A + x_B \ln x_B)$$

$$\text{* Ideal Mixing} \quad \Delta S = k \ln \left(\frac{N_A + N_B}{N_A} \right) \approx -k(N_A + N_B) \left[x_A \ln x_A + x_B \ln x_B \right]$$

$$\underline{\sigma}_i \cdot \left(\frac{N_A + N_B}{N_A} \right) = \underline{\sigma}_f \Rightarrow k(\ln \underline{\sigma}_f - \ln \underline{\sigma}_i) = k \ln \left(\frac{N_A + N_B}{N_A} \right)$$

5. Any Quasistatic Process

$$(1) \quad \Delta T \rightarrow 0, \Delta P \rightarrow 0 \Leftrightarrow (T_B - T_A) \rightarrow 0, (P_B - P_A) \rightarrow 0$$

$$dU = Q + W = Q + (-P \cdot dV)$$

$$\begin{cases} du = T \cdot ds + (-P \cdot dV) \\ W = -PdV \text{ if } P_B = P_A \text{ (quasistatic)} \end{cases}$$

$$\Rightarrow \boxed{Q = T \cdot ds; ds = \frac{Q}{T}} \Rightarrow \Delta S = \begin{cases} \int_{T_i}^{T_f} \frac{C_V dT}{T} \\ \int_{T_i}^{T_f} \frac{C_P dT}{T} \end{cases}$$

$$dS_{\text{total}} = dS_A + dS_B = \frac{Q}{T_A} + \frac{-Q}{T_B}$$

$$(2) \quad \Delta T = (T_B - T_A) \rightarrow 0 \Rightarrow dS_{\text{total}} \rightarrow 0$$

$$\begin{array}{c} \Delta T \rightarrow 0 \Rightarrow \text{When } W=0, dS_{\text{total}} \rightarrow 0. \\ (\times) \text{ Quasistatic} \quad \Delta P \rightarrow 0 \Rightarrow dS_A = \frac{Q}{T_A}; dS_B = \frac{-Q}{T_B} \quad dS_A + dS_B \rightarrow 0. \\ \text{Reversible} \Rightarrow \text{Quasistatic Process} \quad \Delta S = \Delta S_A + \Delta S_B = \frac{Q}{T_A} + \frac{-Q}{T_B} \geq 0 \quad \Delta T \neq 0 \\ \Downarrow \text{A} \sim \text{B interaction.} \quad \text{Reversible } (\Delta S = 0) \Rightarrow \text{Quasistatic} \end{array}$$

$$dS_{\text{total}} = dS_A + dS_B = 0 \quad \text{Irreversible } (\Delta S > 0) \quad \text{Not Quasistatic}$$

$\Delta P = (P_B - P_A) \neq 0$. Not-Quasistatic Process =

$$\begin{aligned} dS_{\text{total}} = dS_A + dS_B &\geq 0 \left(\frac{1}{T_A} - \frac{1}{T_B} \right) > 0 \quad dS_A > \frac{Q}{T_A}; dS_B > \frac{-Q}{T_B} \\ (\because T_A < T_B \therefore \frac{1}{T_A} > \frac{1}{T_B}) \quad \uparrow & \quad \uparrow \end{aligned}$$

$$\Delta T = (T_B - T_A) > 0, W_A > (P_A dV_A); W_B > (-P_B dV_B)$$

Irreversible.

(2)

P_A	P_B
T_A	T_B

设 $P_A < P_B$.

$T_A < T_B$.

$$Q_A + Q_B = 0 \quad Q_A(+), Q_B(-)$$

$$1. P_A \neq P_B \quad dV_A + dV_B = 0 \quad dV_A(-), dV_B(+)$$

$$W_A = P_B \cdot dV_B.$$

$$\downarrow P_B > P_A \text{ 且 } dV_B(+).$$

$$W_A = P_B \cdot dV_B > P_A \cdot dV_B.$$

$$\text{代入 } dV_B = -dV_A.$$

$$W_A = -P_B dV_A > -P_A dV_A.$$

$$W_A > -P_A dV_A.$$

$$W_B = P_A \cdot dV_A.$$

$$\downarrow P_A < P_B \text{ 且 } dV_A(-).$$

$$W_B = P_A \cdot dV_A > P_B dV_A.$$

$$\text{代入 } dV_A = -dV_B.$$

$$W_B = -P_A dV_B > -P_B dV_B.$$

$$W_B > -P_B dV_B.$$

$$\left\{ \begin{array}{l} dU_A = W_A + Q_A. \\ \parallel \quad V \quad \Delta \end{array} \right.$$

$$dU_A = -P_A dV_A + T_A dS_A.$$

$$\left\{ \begin{array}{l} dU_B = W_B + Q_B. \\ \parallel \quad V \quad \Delta \end{array} \right.$$

$$dU_B = -P_B dV_B + T_B dS_B$$

$$T_A \cdot dS_A > Q_A \quad \text{由于 } P_A < P_B \text{ 造成 } T_B dS_B > Q_B.$$

$$dS_A > \frac{Q_A}{T_A} \quad \text{仅当 } P_A = P_B \text{ 时或 } dV=0 \text{ 时 } dS_B > \frac{Q_B}{T_B}.$$

$$\text{取等号 } (P_A = P_B, \text{ 强, 滞, 静态 } (\Delta P \rightarrow 0)).$$

$$P_A \neq P_B$$

$$\updownarrow$$

$$dS_{total} = dS_A + dS_B > \frac{Q_A}{T_A} + \frac{Q_B}{T_B} = \frac{Q_A}{T_A} - \frac{Q_A}{T_B} = Q_A \left(\frac{1}{T_A} - \frac{1}{T_B} \right) > 0$$

$$(Q_A(+)) \text{ 且 } T_A < T_B$$

$$\text{右侧取等号条件: } \left\{ \begin{array}{l} T_A = T_B, \text{ 温度准静态 } (\Delta T \rightarrow 0). \\ \text{或} \end{array} \right.$$

$$\left\{ \begin{array}{l} Q_A = Q_B = 0, \text{ 不传热} \end{array} \right.$$

3. 与可逆的关系

压强准静态

温度准静态

$$dS_{\text{total}} = dS_A + dS_B \geq \frac{Q_A}{T_A} + \frac{Q_B}{T_B} = Q_A \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \stackrel{(1)}{\geq} 0 \quad \stackrel{(2)}{\geq} 0$$

$\Delta P \rightarrow 0 (P_A \approx P_B)$

$\Delta T \rightarrow 0 (T_A \approx T_B)$

(1) 可逆 $\Leftrightarrow dS_{\text{total}} = 0$.

① 处等号成立.

(2) 压强准静态 ($P_A \approx P_B; \Delta P \rightarrow 0$) $\Leftrightarrow dS_A = \frac{Q_A}{T_A}$ 且 $dS_B = \frac{Q_B}{T_B}$.

是可逆的必要条件 (不充分).

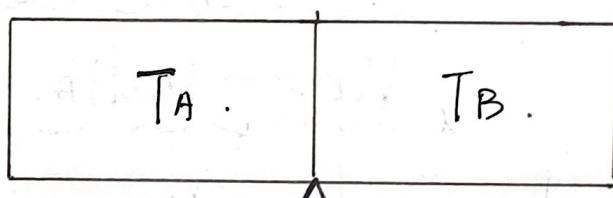
① 处取大于号

(1) 压强非准静态 ($P_A \neq P_B; \Delta P \neq 0$) $\Leftrightarrow dS_A > \frac{Q_A}{T_A}$ 且 $dS_B > \frac{Q_B}{T_B}$.

是不可逆的充分条件 (不必要).

(2) 不可逆 $\Leftrightarrow dS_{\text{total}} > 0$.

举例:



等容. 做体积功.

$T_A < T_B$. 只传热.

$$dS_A = \frac{Q_A}{T_A}, \quad dS_B = \frac{Q_B}{T_B}, \quad Q_A + Q_B = 0.$$

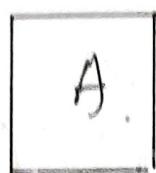
$$dS_{\text{total}} = dS_A + dS_B = \frac{Q_A}{T_A} - \frac{Q_A}{T_B} = Q_A \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \stackrel{(1)}{>} 0$$

不可逆. $\Leftrightarrow dS_{\text{total}} > 0$.

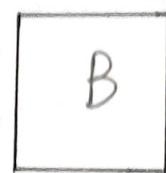
说明 $dS_A = \frac{Q_A}{T_A}; dS_B = \frac{Q_B}{T_B}$ 对于可逆是不充分的.
 $dS_A > \frac{Q_A}{T_A}; dS_B > \frac{Q_B}{T_B}$ 对于不可逆是不必要的.

Entropy Of Mixing

1. A + B.



$$S_A.$$



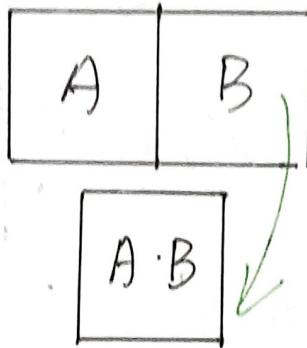
$$S_B.$$

扩散

导致熵增.

$$\Delta S = Nk \ln \frac{V_f}{V_i}$$

$$\Delta S = Nk \ln 2$$



掺入 $\Delta S = 0$.

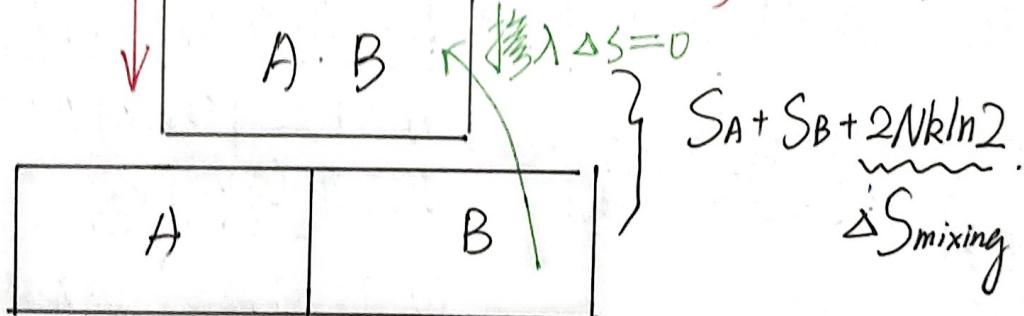
$$S_A + S_B.$$

扩散导致熵增

$$\Delta S = Nk \ln \frac{V_f}{V_i}$$

$$\Delta S = Nk \ln 2$$

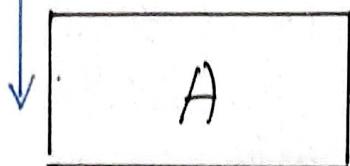
抽去隔板混合导致熵增 $\Delta S_{mixing} = 2Nk \ln 2$



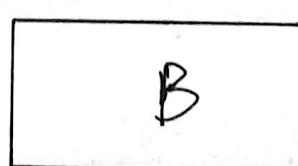
掺入 $\Delta S = 0$

$$S_A + S_B + 2Nk \ln 2$$

$$\Delta S_{mixing}$$



$$S_A + Nk \ln 2$$

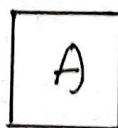


$$S_B + Nk \ln 2$$

A + A.



$$S_A$$



$$S_A$$

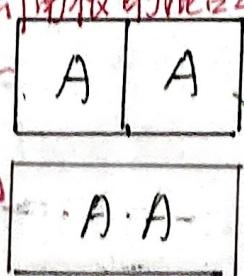
压缩

导致熵减

$$\Delta S = Nk \ln \frac{V_f}{V_i}$$

$$\Delta S = -Nk \ln 2$$

抽去隔板的混合 $\Delta S = 0$



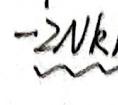
$2S_A$ indistinguishable

压缩导致熵减

$$\Delta S = Nk \ln \frac{V_f}{V_i}$$

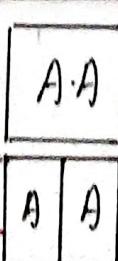
掺入由于重复 $\Delta S = -2Nk \ln 2$

$$\Delta S = -Nk \ln 2$$



$$S_A - Nk \ln 2$$

抽板混合 $\Delta S = 0$



$$S_A - Nk \ln 2$$

有关于温度

(动能)

(一) 确定系统的宏观状态.

① N : 有多少粒子参与构成系统.

② V : 粒子分布的空间范围.

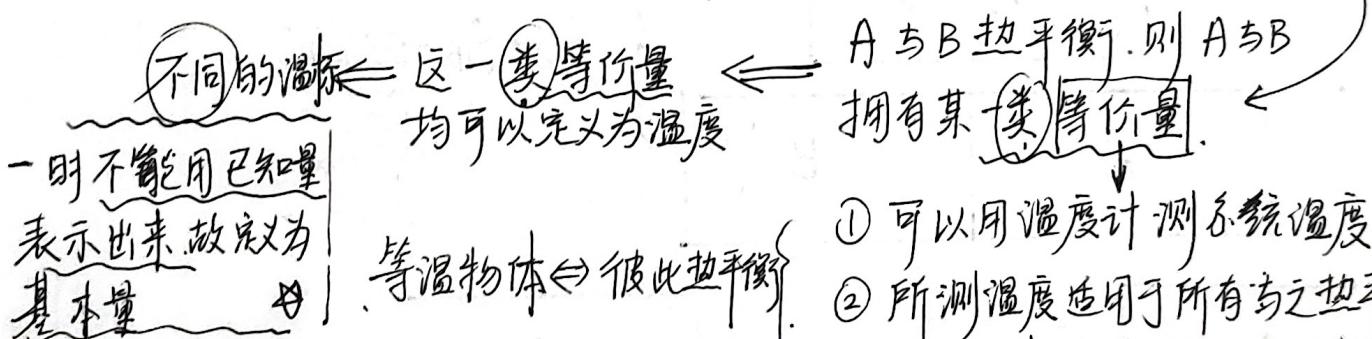
粒子热运动的快慢 E_K
 粒子间相互作用
 (系统内) 总能量 E_P
 (势能)

$$N \quad V \quad U \rightarrow \text{宏观状态} \text{ 的 状态参量} \rightarrow \begin{cases} P = -\left(\frac{\partial U}{\partial V}\right) \\ \mu = \left(\frac{\partial U}{\partial N}\right) \end{cases}$$

* 问题在于内能 U 的“高深莫测”

没有办法把物体内的全部内能转化出来以测量.

* 实验 \Rightarrow 热力学 0th 定律 \Rightarrow 热平衡为一种等价关系.



(二). 从微观分析热平衡.

量子力学 $\Rightarrow \Omega(N, U, V)$ 每个宏观态的微观态数目.

统计学 \Rightarrow 相互作用两物体可取若干宏观态, 最终平衡于 Ω_{max} 的宏观态. (假设每个微观态等概率, $\Omega \uparrow \Rightarrow$ 取到概率大)

$\ln \Omega(N, U, V)$ 是具有可加性的广延量. 定义 $S = k \ln \Omega$.

$$S = k \ln \Omega \quad . \quad S(N, U, V) \Rightarrow \text{热平衡中两物体. } \left(\frac{\partial \ln \Omega}{\partial U}\right)_A = \left(\frac{\partial \ln \Omega}{\partial U}\right)_B$$

↑ 待定系数

$\left(\frac{\partial \ln \Omega}{\partial U}\right)$ 可以定义为温度. 但为了在数值与单位上与现有温标相一致.

$$\text{定义 } \frac{1}{T} = k \left(\frac{\partial \ln \Omega}{\partial U}\right) \Rightarrow T(N, U, V) \Leftrightarrow U(N, T, V), \text{ 以 } T \text{ 代 } U.$$

↑ 可测量

定义系统一. 以 S 为核(心) $\cdot S = S(U, V, N)$.

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}; P = T \left(\frac{\partial S}{\partial V}\right)_{U,N}; \mu = -T \left(\frac{\partial S}{\partial N}\right)_{U,V}.$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN.$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN.$$

$$TdS = dU + PdV - \mu dN.$$

$$\therefore dU = TdS - PdV + \mu dN \quad (*)$$

定义系统二. 以 U 为核(心) $U = U(S, V, N)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN.$$

参考对比 (*) 式.

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}; -P = \left(\frac{\partial U}{\partial V}\right)_{S,N}; \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}.$$

以上表明 定义一 \Leftrightarrow 定义二.

引入 焓 (等压条件反应热). $H = U + PV$.

$$\Delta U = Q + W = Q + (-P\Delta V) \Rightarrow Q = \Delta U + P\Delta V = \Delta H$$

引入 吉布斯自由能 (等压等温条件下判断反应方向). $G = H - TS$.

$$\Delta S \geq \frac{Q}{T} \Leftrightarrow Q - T\Delta S \leq 0 \Leftrightarrow \Delta H - T\Delta S \leq 0 \Leftrightarrow \Delta G \leq 0.$$

(自发).

G 受压强 P 温度 T 影响

物质的量 N 影响
(粒子数)

引入 吉布斯自由能后. G 与其它量的关系.

$$G = H - TS = U + PV - TS.$$

$$dG = \underbrace{dU}_{dU} + \underbrace{Vdp}_{dP} + \underbrace{PdV}_{dV} - \underbrace{sdT}_{dT} - \underbrace{Tds}_{dS}$$

$$\text{代入 (*) 式 } dU + PdV - Tds = \mu dN.$$

数学上对 \downarrow
 $G(P, T, N)$ 的微分.

$$dG = Vdp - sdt + \mu dN. (\#) . \text{ 对比} \quad dG = \left(\frac{\partial G}{\partial P}\right)_{T,V} dp + \left(\frac{\partial G}{\partial T}\right)_{P,V} dt + \left(\frac{\partial G}{\partial N}\right)_{P,T} dN$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T} \because \mu \text{ 是温度压强一定时, 摩尔(对单位物质的量) } G_m.$$

μ . 化学势的三种定义对比.

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{P,T}; \quad \mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V}; \quad \mu = \left(\frac{\partial U}{\partial N} \right)_{S,V}$$

化学中较为熟悉的形式.

$$G = G(T, P, N). : G \text{ 的影响因素.}$$

$T \rightarrow$ 体现在温度. 压强对平衡的影响
 $P \rightarrow$ 体现在化学计量数对 ΔG_m° 的影响
 $N \rightarrow$ 体现在化学计量数对 ΔG_m° 的影响

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P,N} dT + \left(\frac{\partial G}{\partial P} \right)_{T,N} dP + \left(\frac{\partial G}{\partial N} \right)_{T,P} dN.$$

$$dG = -S \cdot dT + V \cdot dP + \mu \cdot dN.$$

$$\therefore \mu = \left(\frac{\partial G}{\partial N} \right)_{P,T}.$$

利用 $G = U + PV - TS$ 定义
 和
 (*) 关键等式
 $dU = TdS - PdV + \mu dN$

即. 在一定压强. 温度下. 单位物质量的吉布斯自由能.

G_m° . 单位: $J \cdot mol^{-1}$.

e.g.



$$\Delta G = p \cdot G_{mX}^{\circ} + q \cdot G_{mY}^{\circ} - m \cdot G_{mA}^{\circ} - n \cdot G_{mB}^{\circ}.$$

$$\Delta G = p \cdot \mu_X^{\circ} + q \cdot \mu_Y^{\circ} - m \cdot \mu_A^{\circ} - n \cdot \mu_B^{\circ}.$$