$\Delta U = Q + W$

热平衡　　力平衡

(T, S)　　(p, V)

强度性质　　广度性质

化学平衡是内平衡

力平衡和热平衡是环境—系统平衡

强度性质是能量对于共轭广度性质的偏微分

每一个平衡需要一对共轭状态函数来描述

这两组基本变量不能直接计算做功，传热，是从系统本身出发，衡量做功和传热的系统内在效应

对于组分不变的均匀封闭系统，各组分物质的量可作为描述系统大小的基本变量

单一组分均匀封闭系统的一个状态 —— 3个独立变量 (T, p)

C个组分，均匀封闭，组分之间无关联关系 —— $C+2$ 个独立变量

组分不变、非机械功=0 的封闭系统中状态函数的变化量需两个独立变量来确定

T　S　p　V

(T, p)　(T, V)　(S, p)　(S, V)　独立基本变量组

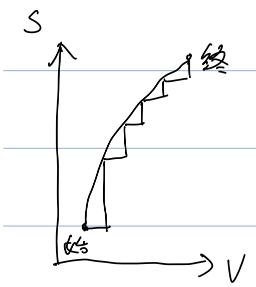
$\downarrow$　$\downarrow$　$\downarrow$　$\downarrow$

G　A　H　U

热力学基本方程

$U = f(V, S, n_1, n_2, \cdots n_c)$　组分不变的均匀封闭系统

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



拆分为数个微等S过程和微等V过程

微等V可逆过程：只有微小可逆热　$dS = \frac{dQ_{可逆}}{T}$

微等S可逆过程：内能变化完全来源于微小可逆功

$$dS = \frac{dU}{T} + \frac{pdV}{T} = 0$$

热力学基本方程 $dU = dq_{可逆} + dw_{可逆} = TdS - PdV$

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

温度是单位熵变所需要的能量，是系统熵改变的难易程度

基本公式不是第一定律和第二定律的结合，绝热是系统内部变化的过程

$H = U + PV \qquad dH = dU + PdV + VdP = TdS + VdP$

H对应的基组为 (S,P) $\qquad T = \left(\frac{\partial H}{\partial S}\right)_{P,n} \qquad V = \left(\frac{\partial H}{\partial P}\right)_{S,n}$

$A = U - TS \qquad dA = dU - TdS - SdT = -SdT - PdV$

A对应的基组为 (T,V) $\qquad -S = \left(\frac{\partial A}{\partial T}\right)_{V,n} \qquad -P = \left(\frac{\partial A}{\partial V}\right)_{T,n}$

$G = H - TS \qquad dG = dH - TdS - SdT = -SdT + VdP$

G对应基组为 (T,P) $\qquad -S = \left(\frac{\partial G}{\partial T}\right)_{P,n} \qquad V = \left(\frac{\partial G}{\partial P}\right)_{T,n}$

(P,V) 和 (T,S) 不能构建能量类函数

麦克斯韦方程

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

$$\left(\frac{\partial V}{\partial S}\right)_{P,n} = \left(\frac{\partial T}{\partial P}\right)_{S,n} \qquad H$$

$$\left(\frac{\partial P}{\partial T}\right)_{V,n} = \left(\frac{\partial S}{\partial V}\right)_{T,n} \qquad A$$

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

压力的热力学诠释

$$-P = \left(\frac{\partial A}{\partial V}\right)_{T,n} \qquad P = -\frac{\partial (U-TS)}{\partial V} = T\left(\frac{\partial S}{\partial V}\right)_{T,n} - \left(\frac{\partial U}{\partial V}\right)_{T,n}$$

压强不只是决定于 $\frac{\partial U}{\partial V}$，也决定于 $\frac{\partial S}{\partial V}$

理想气体

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = T\left(\frac{\partial S}{\partial V}\right)_{T,n} - P$$

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = T\left(\frac{\partial p}{\partial T}\right)_{V,n} - p = T\left[\frac{\partial(nRT/V)}{\partial T}\right]_{V,n} - p$$

$$= \frac{nRT}{V} - p = 0$$ 理想气体内能与V无关，只与T有关

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT \equiv C_V dT$$

$$\left(\frac{\partial H}{\partial p}\right)_{T,n} = \left(\frac{\partial G}{\partial p}\right)_{T,n} + T\left(\frac{\partial S}{\partial p}\right)_{T,n} = V - T\left(\frac{\partial V}{\partial T}\right)_{p,n} = V - \frac{nRT}{p} = 0$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_{p,n} dT = C_p\, dT$$ H与p无关，只与T有关

$$C_p dT = dH = d(U+pV) = C_V dT + nR dT$$

$$\therefore C_p = C_V + nR$$