常数表，字母记号

$N_A = 6.022 \times 10^{23}\,mol^{-1}$

$R = 8.3149\,J\cdot mol^{-1}\cdot k^{-1} \approx 2\,cal\,mol^{-1}\cdot k^{-1}$

$k = \frac{R}{N_A} = 1.380662 \times 10^{-23}\,J\cdot k^{-1}$

1u（原子质量单位）　$1.6605 \times 10^{-27}\,kg$

n：单位体积分子数（分子数密度，单位：个）

m：单个分子质量　　M：（气体，固体）总质量

$1atm = 1.013 \times 10^5\,Pa$　　N：总分子数

标况1mol 理想气体体积 $V_0 = 22.41\,L\cdot mol^{-1}$

ν：摩尔数　　$(n = \frac{N_A}{V_0})$ → 气：$10^{19}\,cm^{-3}$　固液：$10^{22\sim23}\,cm^{-3}$

$V = \nu V_0$

μ 摩尔质量 $(kg\cdot mol^{-1})$

$p = \frac{1}{3} n m \bar{v}^2 = \frac{1}{3}\rho \bar{v}^2$　　$\rho = \frac{\mu}{V_0} = \frac{\mu\cdot\nu}{V_0\,\nu} = \frac{N\cdot m}{V} = n\cdot m$

$\bar{v} \approx \sqrt{\frac{3P}{nm}}$

碰壁数 $\Gamma \approx \frac{1}{6} n\bar{v}$　$(= \frac{1}{4} n\bar{v})$

碰撞频率 $Z = \sqrt{2}\pi d^2 n \bar{v}$　　d为分子有效直径

平均自由程 $\bar{\lambda} = \frac{\bar{v}}{Z} = \frac{1}{\sqrt{2} n \pi d^2}$

第0定律　A,B 同时与C热平衡 ⇒ A,B也热平衡

$pV = \nu RT = NkT$，$P = nkT$

实际气体

$(p + \frac{\nu^2 a}{V^2})(V - \nu b) = \nu RT$　ν为摩尔数

由 $f(p,V,T) \equiv 0$，∴$V(p,T)$，得

$dV = (\frac{\partial V}{\partial p})_T dp + (\frac{\partial V}{\partial T})_p dT$

记等压 体积膨胀　$\alpha = \frac{1}{V}(\frac{\partial V}{\partial T})_p$

等温　$\beta = -\frac{1}{V}(\frac{\partial V}{\partial p})_T$

$\therefore \frac{dV}{V} = \alpha dT - \beta dp$

d.热一及应用

$dQ = pdV + dU$

$dV = 0$，恒容　$\therefore C_V = (\frac{dQ}{dT})_V = (\frac{dU}{dT})_V$

$dp = 0$，恒压　$\therefore C_p = (\frac{dQ}{dT})_p = \frac{d(U+pV)}{dT} = \frac{dH}{dT}$

焓：$H = U + pV$

又 $pV = \nu RT$

$\therefore C_p = C_V + \nu R$（理想气体）　$C_{p,m} = C_{V,m} + R$（1mol 时）

记热容比 $\gamma = \frac{C_p}{C_V} = \frac{C_{p,m}}{C_{V,m}} > 1$

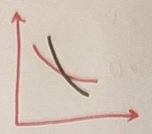
$Q = \int_{T_i}^{T_f} C_n dT$　（由 $C = \frac{dQ}{dT}$ 还原）

绝热方程

$pV^{\gamma} = C_1$，$TV^{\gamma-1} = C_2$，$P^{\gamma-1}T^{-\gamma} = C_3$

绝热系统对外做功

V_1 到 V_2　$-\int_{V_1}^{V_2} pdV = \frac{p_1V_1 - p_2V_2}{\gamma - 1}$



$$pV^n = C \begin{cases} n=0 & 等压 \\ n=1 & 等温 \\ n=\gamma & 绝热 \\ n=\infty & 等容 \end{cases}$$

$$\gamma = \begin{cases} \frac{5}{3} & 单原子分子 \\ \frac{7}{5} & 双 \\ \frac{4}{3} & 多 \end{cases}$$

焦汤系数 $\alpha_i = (\frac{\partial T}{\partial p})_H$　（理想气体，$\alpha_i = 0$）

$(dH = (\frac{\partial H}{\partial T})_p dT + (\frac{\partial H}{\partial p})_T dp$ ），$dH = 0$，$\frac{dT}{dp} = -\frac{(\frac{\partial H}{\partial p})_T}{\boxed{(\frac{\partial H}{\partial T})_p}}$，$\boxed{(\frac{\partial H}{\partial T})_p} = C_p$

$= -\frac{1}{C_p}\left[\frac{\partial(U+pV)}{\partial p}\right] = -\frac{1}{C_p}\left[(\frac{\partial U}{\partial p})_T + p(\frac{\partial V}{\partial p})_T + V\right]$

$= -\frac{1}{C_p}\left[(\frac{\partial U}{\partial V})_T(\frac{\partial V}{\partial p})_T + V + p(\frac{\partial V}{\partial p})_T\right]$

一般 p-V 系统 U与V存在：

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

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

$f(x,y,z) = 0$，$(\frac{\partial x}{\partial y})_z(\frac{\partial y}{\partial z})_x(\frac{\partial z}{\partial x})_y = -1$

$= -\frac{1}{C_p}\left[T\frac{-1}{(\frac{\partial T}{\partial V})_p} + V\right] = -\frac{1}{C_p}\left[V - T(\frac{\partial V}{\partial T})_p\right]$

$\alpha_i = 0$　对反转曲线　　对于实际气体

$T = \frac{2a(V-b)^2}{RbV^2}$　　$T_{max} = \frac{2a}{Rb}$

热机/制冷机

$\eta = \frac{W'}{Q_1} = 1 - \frac{Q_2}{Q_1}$（p,V图顺时针）　本质：工作物质（气体）对外做功 W' 占从高温热源吸收的热量 Q_1 的比例

若有两段绝热，多用②

$\varepsilon = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$（p,V图逆时针）　从低温物体吸收的 Q_2 与消耗的功 W 的比值

$\eta \le 1 - \frac{T_2}{T_1}$（卡诺热机取等）　　$\varepsilon \le \frac{T_2}{T_1 - T_2}$（卡诺冷机取等）

热二与熵

理想气体. $V_1 \to V_2$

过程	Q	W(外对气体) $-pdV$	U	ΔS
恒T	$-W$	$\nu RT\ln\frac{V_2}{V_1}$	0	
P	$C_p dT$	$-p(V_2-V_1)$	$W+Q$	
V	$C_V dT$	0	$C_V dT$	
可逆绝热膨胀	0			0
绝热自由	0			>0
绝热节流	0			>0

一般 $p\sim V$ U与V关系 $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$

C_p与C_V关系 $C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)\left(\frac{\partial V}{\partial T}\right)_p$

理想气体，U只与T有关 $U(T)$.

理想：$\Delta S = C_V\ln\frac{T}{T_0} + \nu R\ln\frac{V}{V_0}$ $S(T,V)$

$= C_p\ln\frac{T}{T_0} - \nu R\ln\frac{p}{p_0}$ $S(T,p)$

$= C_V\ln\frac{p}{p_0} + C_p\ln\frac{V}{V_0}$ $S(V,p)$

实际分 $\Delta S = C_V\ln\frac{T}{T_0} + R\ln\frac{V-\nu b}{V_0-\nu b}$

$=$ 或 $R\ln\frac{v-b}{v_0-b}$ v为1mol气体的体积

由 $dS = \frac{dQ}{T}$, $dQ = dU + pdV$

$TdS = dU + pdV$ 若 $S(U,V)$

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

$= \frac{1}{T}dU + \frac{p}{T}dV$ $\Rightarrow T = \frac{\partial U}{\partial S}$

麦克斯韦分布

$\begin{cases} p = \frac{2}{3}n\bar{\varepsilon}_k \\ p = nkT \end{cases} \Rightarrow \begin{cases} \bar{\varepsilon}_k = \frac{3}{2}kT \\ T = \frac{2}{3k_B}\bar{\varepsilon}_k \end{cases}$

而 $\bar{\varepsilon} = \frac{1}{2}m\bar{v}^2$, $\sqrt{\bar{v^2}} = \sqrt{\frac{3RT}{\mu}}$

$f(v_x,v_y,v_z) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m}{2kT}v^2}$, $v^2 = v_x^2+v_y^2+v_z^2$

θ,φ为$\vec{v}$的方向

$f(v)dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m}{2kT}v^2}\cdot v^2$.

在 $v_2\sim v_1$ 内，若 $\Delta V = V_2 - V_1$ 相比V_1很小

$\Delta N = N\cdot 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\int_{v_1}^{v_2} e^{-\frac{m}{2kT}v^2}v^2 dv$

$\approx N\cdot 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m}{2kT}v_1^2} v_1^2\Delta V$

碰壁数 $\Gamma = \frac{1}{4}n\bar{v}$

$\bar{v} = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\int_0^{\infty} v\, e^{-\frac{m}{2kT}v^2}v^2 dv = \sqrt{\frac{8RT}{\pi\mu}}$

$f'(v)=0$, 得 v_p(最概然速率) $= \sqrt{\frac{2RT}{\mu}}$

$v_p : \bar{v} : \sqrt{\bar{v^2}} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$

$\sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi\mu}}$

$\bar{\varepsilon}_k$(分子平动能) $= \frac{3}{2}kT$ 各个方向 $\frac{1}{2}kT$

平衡态下，分子每个自由度有相同平均动能，大小 $\frac{1}{2}kT$

t个平动自由度，r个转动自由度，s个振动自由度

$\bar{\varepsilon} = (t+r+2s)\frac{1}{2}kT$
- 单原子 $t=3, r=s=0$ $\frac{3}{2}kT$
- 双 $t=3, r=2, s=1$ $\frac{7}{2}kT$
- 多 $t=3, r=3, s=3n-6$

理想气体只与T有关

$U = N\bar{\varepsilon} = \frac{1}{2}(t+r+2s)NkT = \frac{1}{2}(t+r+2s)\nu RT$

$C_V = \frac{dU}{dT}$ 单原子：$\frac{3}{2}R$，接近.

双原子：
- 极低温 $\frac{3}{2}R$ 无转动，振动
- 常温 $\frac{5}{2}R$ 无振动
- 高温 $\frac{7}{2}R$

麦克斯韦关系

① $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$ $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$ $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$ $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right.$

用 $TdS = dU + pdV$ 证明

① $dU = TdS - pdV$

$= \left(\frac{\partial U}{\partial S}\right)dS + \left(\frac{\partial U}{\partial V}\right)dV$ $\begin{cases} T = \frac{\partial U}{\partial S} \\ -p = \frac{\partial U}{\partial V} \end{cases}$ 由 $\frac{\partial^2 U}{\partial V\partial S} = \frac{\partial^2}{\partial S}$ 知 $\left(\frac{\partial T}{\partial V}\right)_S = -($

范式熵变

$dQ = dU + pdV = \left(\frac{\partial U}{\partial T}\right)dT + \left(\frac{\partial U}{\partial V}\right)dV + pdV$ 代入 $\left(\frac{\partial U}{\partial V}\right) = T\left(\frac{\partial p}{\partial T}\right)$

$= \left(\frac{\partial U}{\partial T}\right)dT + T\left(\frac{\partial p}{\partial T}\right)dV$ $\therefore \frac{dQ}{T} = C_V\frac{dT}{T} + \left(\frac{\partial p}{\partial T}\right)dV$

$p = \frac{RT}{V-\nu b} - \frac{n^2 a}{V^2}$ $\frac{\partial p}{\partial T} = \frac{R}{V-\nu b}$

$\int_{(T_0,V_0)}^{(T,V)} = \int_{(T_0,V_0)}^{(T,V_0)} + \int_{(T,V_0)}^{(T,V)} = C_V\ln\frac{T}{T_0} + R\ln\frac{(V-\nu b)}{V_0-\nu b}$

$C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p$