大物真经

Wbx

热学

浙江大学 ZHEJIANG UNIVERSITY

两个假设

Tips: 大物这一章物理量及其对应的符号一定要分清

1. 分子数密度 $n=\frac{dN}{dV}$ 处处相等
2. 速度的平均值 $\bar{v}_x=\frac{1}{N}\sum_{i=1}^{N}\bar{v}_{ix}$ 各方向运动概率相等 $\bar{v}_{ix}=\bar{v}_{iy}=\bar{v}_{iz}=0$

引入：速度平方的平均值 $\overline{v_x^2}=\frac{1}{N}\sum_{i=1}^{N}v_{ix}^2$ $\quad \overline{v_x^2}=\overline{v_y^2}=\overline{v_z^2}=\frac{1}{3}\overline{v^2}$

压强 $p=\frac{\bar{F}}{S}=\frac{\sum f\Delta t}{\Delta t S}$ $\quad p=\frac{1}{3}n\mu\overline{v^2}=\frac{2}{3}n\cdot\frac{1}{2}\mu\overline{v^2}=\frac{2}{3}n\bar{\varepsilon}_t$ 平均平动动能

推导：$I_{i1}=-2\mu v_{ix}$（μ：单个分子质量）

对面的冲量 $I_{i1}=2\mu v_{ix}$

$T_i=\frac{2x}{v_{ix}}\quad z_i=\frac{t}{T_i}=\frac{v_{ix}t}{2x}$

$I_{isum}=z_iI_i=\frac{v_{ix}t}{2x}\cdot 2\mu v_{ix}=\frac{\mu t}{x}v_{ix}^2$

$I_{sum}=\sum_{i=1}^{N}\frac{\mu t}{x}v_{ix}^2$

$\bar{F}=\frac{I_{sum}}{t}=\sum_{i=1}^{N}\frac{\mu}{x}v_{ix}^2$

$p=\frac{\bar{F}}{S}=\frac{1}{yz}\sum_{i=1}^{N}\frac{\mu}{x}v_{ix}^2=\frac{1}{xyz}\sum_{i=1}^{N}\mu v_{ix}^2=\frac{1}{V}\mu\sum_{i=1}^{N}v_{ix}^2=\frac{N}{V}\mu\cdot\left(\frac{1}{N}\sum_{i=1}^{N}v_{ix}^2\right)$

$=n\cdot\mu\cdot\overline{v_x^2}=\frac{1}{3}n\mu\overline{v^2}$

$pV=\frac{m}{M}RT=\nu RT$ （$R=8.31\,J\cdot mol^{-1}\cdot K^{-1}$ 普适气体常量 or 摩尔气体常量）

$\nu=\frac{m}{M}=\frac{N}{N_A}$ （M：摩尔质量 kg/mol）

$p=\frac{1}{V}\cdot\frac{N}{N_A}\cdot R\cdot T=\frac{N}{V}\cdot\frac{R}{N_A}\cdot T=n\cdot k\cdot T$ （$k=1.38\times10^{-23}\,J\cdot K^{-1}$ 玻尔兹曼常量）

$\begin{cases}p=nkT\\ p=\frac{2}{3}n\bar{\varepsilon}_t\end{cases}\Rightarrow\bar{\varepsilon}_t=\frac{3}{2}kT$ （$T=t+273.15$）

$\bar{\varepsilon}_t = \frac{3}{2}kT = \frac{1}{2}\mu\bar{v^2} \Rightarrow \sqrt{\bar{v^2}} = \sqrt{\frac{3kT}{\mu}} = \sqrt{\frac{3RT}{M}}$ ($R = N_A k$)

自由度

- 单原子分子 $i=3$
- 刚性双原子分子 $i=5$
- 刚性多原子分子 $i=6$

能量均分：分子热运动的每一个平均自由度的平均动能均等于 $\frac{1}{2}kT$

分子自由度 $i \Rightarrow$ 平均动能 $\bar{\varepsilon} = \frac{i}{2}kT$

ν mol 理想气体内能

$\bar{E} = \nu N_A \cdot (\frac{i}{2}kT) = \nu \cdot \frac{i}{2}RT = \frac{i}{2}PV$

$\frac{RT}{M} = \frac{PV}{m} = \frac{P}{\frac{m}{V}} = \frac{P}{\rho}$ (题目涉及密度 ρ 可用)

速率分布函数

$dN = N_0 f(v)\, dv$ (N_0: 分子数)　　$f(v) = \frac{dN}{N_0 dv}$

- $f(v)\, dv = \frac{dN}{N_0}$　　占总分子数的百分比
- $N_0 f(v)\, dv = dN$　　在 $v \sim v+dv$ 内的分子数
- $\int_{v_1}^{v_2} f(v)\, dv$　　曲线下的面积；百分比 or 概率
- $\int_0^{\infty} f(v)\, dv = 1$　　归一化条件

最概然速率 v_p (most probable speed)

$\left.\frac{df}{dv}\right|_{v=v_p} = 0$

平均速率

$\bar{v} = \frac{1}{N_0}\int_0^{N_0} v\, dN = \frac{1}{N_0}\int_0^{\infty} v N_0 f(v)\, dv = \int_0^{\infty} v f(v)\, dv$

方均根速率 $\sqrt{\bar{v^2}}$

$\bar{v^2} = \frac{1}{N_0}\int_0^{N_0} v^2 dN = \frac{1}{N_0}\int_0^{\infty} v^2 N_0 f(v)\, dv = \int_0^{\infty} v^2 f(v)\, dv$

介于 $v_1 \sim v_2$ 之间电子的

平均速率：$\overline{v_{12}} = \dfrac{\int_{v_1}^{v_2} v\,dN}{\int_{v_1}^{v_2} dN} = \dfrac{\int_{v_1}^{v_2} v f(v)\,dv}{\int_{v_1}^{v_2} f(v)\,dv}$

方均根速率 $\sqrt{\overline{v_{12}^2}} = \sqrt{\dfrac{\int_{v_1}^{v_2} v^2 N_0 f(v)\,dv}{\int_{v_1}^{v_2} N_0 f(v)\,dv}} = \sqrt{\dfrac{\int_{v_1}^{v_2} v^2 f(v)\,dv}{\int_{v_1}^{v_2} f(v)\,dv}}$

麦克斯韦速率分布（那一坨不用记）

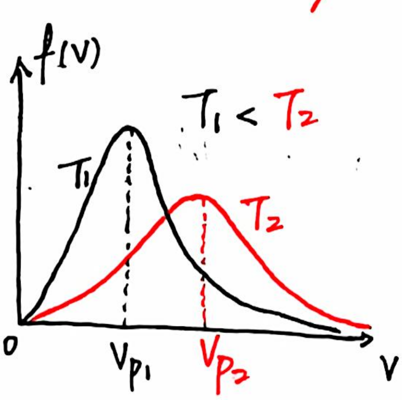
推导：令 $b = \dfrac{\mu}{2kT}$ 代入 $\left.\dfrac{df}{dv}\right|_{v=v_p} = 0 \Rightarrow v_p = \sqrt{b}$

代入 $\bar{v} = \dfrac{1}{N_0}\int_0^{N_0} v\,dN \Rightarrow \bar{v} = 2\sqrt{\dfrac{1}{b\pi}}$

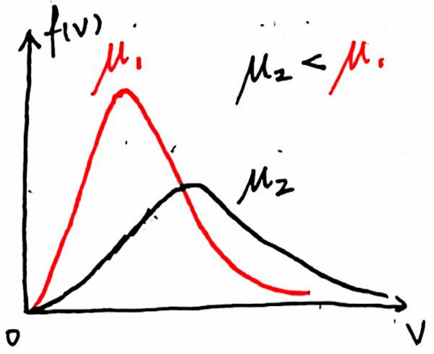
代入 $\sqrt{\overline{v^2}} = \sqrt{\dfrac{1}{N_0}\int_0^{N_0} v^2\,dN} \Rightarrow \sqrt{\overline{v^2}} = \sqrt{\dfrac{3}{2b}}$

$$\begin{cases} v_p = \sqrt{\dfrac{2kT}{\mu}} = \sqrt{\dfrac{2RT}{M}} \\ \bar{v} = \sqrt{\dfrac{8kT}{\pi\mu}} = \sqrt{\dfrac{8RT}{\pi M}} \\ \sqrt{\overline{v^2}} = \sqrt{\dfrac{3kT}{\mu}} = \sqrt{\dfrac{3RT}{M}} \end{cases}$$

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

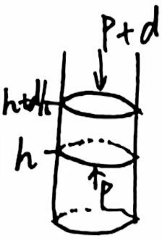


温度越高
分子热运动越强烈



分子质量越小
分子越容易运动

等温气压公式 $p=p_0 e^{-\frac{\mu g h}{RT}} = p_0 e^{-\frac{\varepsilon_p}{RT}}$



$$[pS-(p+dp)S]-\rho g S dh=0 \Rightarrow -dp=\rho g dh$$

$$\rho=\frac{pM}{RT} \qquad -dp=\frac{pM}{RT}g\,dh \Rightarrow \frac{dp}{p}=-\frac{Mg}{RT}dh$$

$$\int_{p_0}^{p}\frac{dp}{p}=\int_0^h -\frac{Mg}{RT}dh \Rightarrow \frac{p}{p_0}=e^{-\frac{Mgh}{RT}}$$

分子数密度按高度分布

$n=\frac{p}{kT}=\frac{p_0}{kT}e^{-\frac{\varepsilon_p}{kT}}$ （$\frac{p_0}{kT}=n_0$ $h=0$处的分子数密度）

碰撞频率 $\bar{z}$

其他分子静止 $dV=\bar{v}_r\,dt\,\sigma$ $\sigma=\pi d^2$ $dN=n\,dV=n\bar{v}_r\,dt\,\sigma$

$\bar{z}=\frac{dN}{dt}=n\bar{v}_r\sigma=n\bar{v}_r\pi d^2$ （$\bar{v}_r=\sqrt{2}\bar{v}$）

其他分子也动 $\bar{z}=\sqrt{2}\pi d^2\bar{v}n$

特别地，若为电子 $\bar{z}=\frac{1}{4}n\pi d^2\bar{v}_e$

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

范德瓦尔斯方程

$$\left(p+a\frac{\nu^2}{V^2}\right)(V-\nu b)=\nu RT$$

a: 压强修正值
b: 1mol气体分子的体积，体积修正值

热力学第一定律: $\Delta E=\underbrace{Q}_{\text{外界传递热量}}+\underbrace{A}_{\text{外界对系统做功}}$ $dQ=dE+(-dA)$

做功 $-A=\int_{V_1}^{V_2}p\,dV$

$$\Delta E=\nu\cdot\frac{i}{2}RT_2-\nu\cdot\frac{i}{2}RT_1=\nu\cdot\frac{i}{2}R\Delta T=\frac{m}{M}\cdot\frac{i}{2}R\Delta T=\frac{i}{2}(p_2V_2-p_1V_1)$$

$$dE=\nu\cdot\frac{i}{2}R\,dT=\frac{m}{M}\frac{i}{2}R\,dT \qquad Q=\Delta E+(-A)=\nu\cdot\frac{i}{2}R\Delta T+\int_{V_1}^{V_2}p\,dV$$

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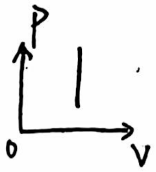
热容 $C=\frac{dQ}{dT}$　　比热 $c=\frac{dQ}{mdT}=\frac{C}{m}$

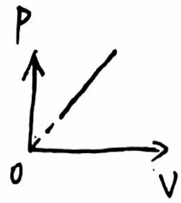
$dQ=mcdT=\int_{T_1}^{T_2}mcdT=mc\Delta T$

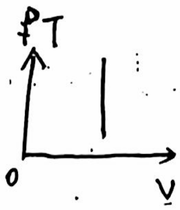
摩尔热容 $C_{l,m}=\frac{dQ}{\nu dT}=\frac{C}{\nu}=\frac{C}{\frac{m}{M}}=cM$　　1mol物质T↑1k所吸收的热量

$Q_l=\int_{T_1}^{T_2}\nu C_{l,m}dT$

等体过程 $V=Const$　$\frac{P}{T}=PT^{-1}=\frac{\nu R}{V}$







$(-A_V)=0$ (体积无变化)

$\Delta E=\nu\cdot\frac{i}{2}R\cdot\Delta T$　　$Q=\Delta E+(-A_V)=\Delta E$

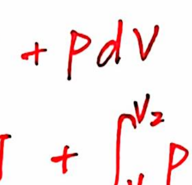
定体摩尔热容 $C_{V,m}=\frac{i}{2}R$

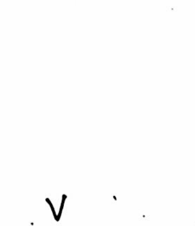
$dE=\nu\cdot\frac{i}{2}R\,dT=\nu C_{V,m}dT$

$dQ=dE+(-dA)=\nu\cdot C_{V,m}dT+PdV$

$Q=\Delta E+(-A)=\int_{T_1}^{T_2}\nu C_{V,m}dT+\int_{V_1}^{V_2}PdV$

等压过程 $dp=0$　$\frac{V}{T}=\frac{\nu R}{P}=Const$





$(-A_p)=\int_{V_1}^{V_2}PdV=P(V_2-V_1)=\nu R(T_2-T_1)$

$\Delta E=\nu\cdot\frac{i}{2}R\Delta T=\nu\cdot\frac{i}{2}R(T_2-T_1)=\nu C_{V,m}(T_2-T_1)$

$Q=\Delta E+(-A_p)=\nu\cdot(C_{V,m}+R)(T_2-T_1)$

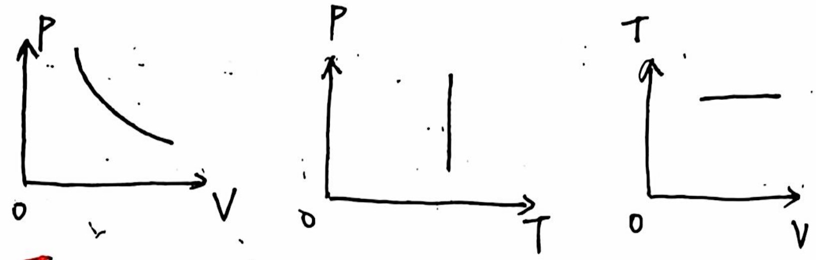
定压摩尔热容 $C_{p,m}=\frac{dQ_p}{\nu dT}=C_{V,m}+R=\frac{i}{2}R+R=(\frac{i}{2}+1)R$

定压摩尔热容计算等压过程

$Q_p = \nu C_{p,m} dT$ $\quad$ $Q_p = \int_{T_1}^{T_2} \nu C_{p,m} dT$

摩尔热容比 $\gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{C_{V,m}+R}{C_{V,m}} = 1 + \frac{R}{C_{V,m}} = 1 + \frac{2}{i}$ $\quad$ $\gamma - 1 = \frac{R}{C_{V,m}}$

等温过程 $pV = \nu RT = Const$



$\Delta E = \nu \frac{i}{2} R \Delta T = \nu C_{V,m} \Delta T = 0$

$Q_T = -A_T = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \frac{\nu RT}{V} dV = \nu RT \ln\frac{V_2}{V_1} = \nu RT \ln\frac{p_1}{p_2}$

等温摩尔热容 $C_{T,m} = \frac{dQ}{\nu dT} \to +\infty$

绝热过程 $Q = 0$

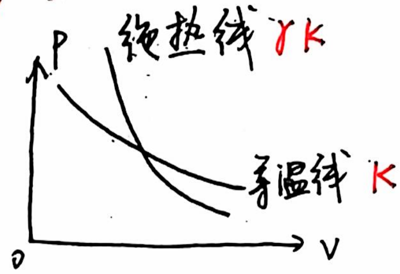
$-dA = pdV$ $\quad$ $dE = \nu C_{V,m} dT$ $\quad$ $0 = dE + (-dA)$

$pV = \nu RT \to \nu R dT = pdV + Vdp$

$\nu C_{V,m} dT + pdV = 0$

$\Rightarrow \frac{dp}{p} + \gamma \frac{dV}{V} = 0$

$\Rightarrow pV^{\gamma} = C_1$ $\quad$ $TV^{\gamma-1} = C_2$ $\quad$ $p^{\gamma-1} T^{-\gamma} = C_3$



$Q = 0$

$pV^{\gamma} = p_1 V_1^{\gamma} = p_2 V_2^{\gamma} \to p = p_1 V_1^{\gamma} V^{-\gamma}$

$-A_Q = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} p_1 V_1^{\gamma} V^{-\gamma} dV = \frac{\Delta(pV)}{1-\gamma} = \frac{p_2V_2 - p_1V_1}{1-\gamma}$

$Q = \Delta E + (-A_Q) = 0 \Rightarrow -A_Q = -\Delta E = -\nu C_{V,m} \Delta T$

$\Delta E = A_Q = \frac{p_2V_2 - p_1V_1}{\gamma - 1}$

绝热摩尔热容 $C_{Q,m} = \frac{dQ}{\nu dT} = 0$ $\quad$ $C_{V,m} = \frac{R}{\gamma-1}$

多方过程 $pV^n = Const$ $\quad$ n: 多方指数

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$PV^n = P_1V_1^n = P_2V_2^n$

$-A_n = \frac{P_2V_2 - P_1V_1}{1-n} = \frac{\nu R\Delta T}{1-n}$ $\Delta E = \nu C_{V,m}\Delta T$

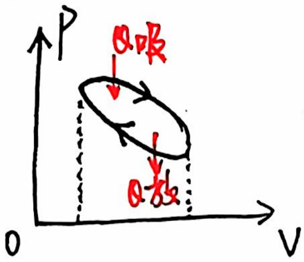
$Q_n = \Delta E + (-A_n) = \nu \cdot \frac{n-\gamma}{n-1} C_{V,m}\Delta T$

$C_{n,m} = \frac{dQ_n}{\nu dT} = \frac{n-\gamma}{n-1} C_{V,m}$

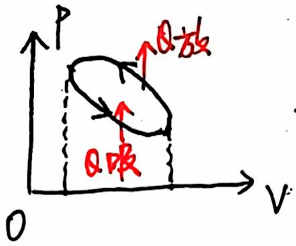
$Q_n = \int_{T_1}^{T_2} \nu C_{n,m} dT = \nu C_{n,m}\Delta T = \nu \cdot \frac{n-\gamma}{n-1} C_{V,m}\Delta T$

循环过程

$\Delta E = 0$ $Q = \Delta E + (-A) = -A$ 顺时针为正循环



$-A = Q_{吸} - |Q_{放}| > 0$ 正循环

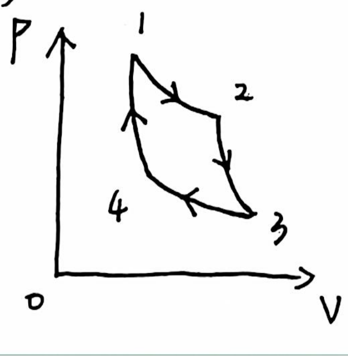


$-A = Q_{吸} - |Q_{放}| < 0$ 逆循环

正循环 → 热机 $\eta = \frac{-A}{Q_{吸}} = \frac{Q_{吸} - |Q_{放}|}{Q_{吸}} = 1 - \frac{|Q_{放}|}{Q_{吸}}$

逆循环 → 制冷机 $e = \frac{Q_{吸}}{A} = \frac{Q_{吸}}{|Q_{放}| - Q_{吸}}$

卡诺循环



1→2 等温膨胀 $Q_{12} = \nu RT_1 \ln\frac{V_2}{V_1} > 0$ 吸热

2→3 绝热膨胀 $Q_{23} = 0$ $T_1V_2^{\gamma-1} = T_2V_3^{\gamma-1}$

3→4 等温压缩 $Q_{34} = \nu RT_2 \ln\frac{V_4}{V_3} < 0$ 放热

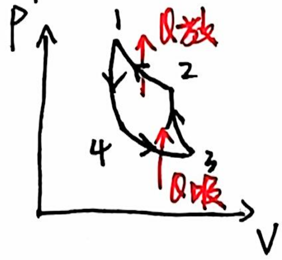
4→1 绝热压缩 $Q_{41} = 0$ $T_1V_1^{\gamma-1} = T_2V_4^{\gamma-1}$

$\frac{V_2}{V_1} = \frac{V_3}{V_4}$

$$\eta_c = \frac{-A}{Q_{吸}} = 1 - \frac{\nu R T_2 \ln\frac{V_3}{V_4}}{\nu R T_1 \ln\frac{V_2}{V_1}} = 1 - \frac{T_2}{T_1}$$

$$-\frac{Q_{T_2}}{T_2} = \frac{Q_{T_1}}{T_1} \Rightarrow \frac{Q_{T_1}}{T_1} + \frac{Q_{T_2}}{T_2} = 0$$ 克劳修斯等式 $\oint_L \frac{dQ}{dT} = 0$

制冷（略）



$Q_{吸} = Q_{43}$

$Q_{放} = Q_{21}$

$$e = \frac{Q_{吸}}{A} = \frac{Q_{吸}}{|Q_{放}| - Q_{吸}} = \frac{T_2}{T_1 - T_2}$$

熵 $\oint \frac{dQ}{dT} = 0$ 卡诺循环中，$\frac{dQ}{T}$ 总和为0

$dS = \frac{dQ}{T}$ (J/k) $\quad dQ = TdS \quad Q = \int_{S_1}^{S_2} T\,dS$

$dQ = TdS = dE + (-dA) = dE + pdV$

绝热可逆 $dS = \int_a^b \frac{dQ}{T} = 0$ 等熵过程

等体可逆 $\Delta S = \int_a^b \frac{dQ_V}{T} = \int_{T_1}^{T_2} \frac{\nu C_{V,m} dT}{T} = \nu C_{V,m} \ln\frac{T_2}{T_1}$

等压可逆 $\Delta S = \int_a^b \frac{dQ_p}{T} = \int_{T_1}^{T_2} \frac{\nu C_{p,m} dT}{T} = \nu C_{p,m} \ln\frac{T_2}{T_1}$

等温可逆 $\Delta S = \int_a^b \frac{dQ_T}{T} = \frac{Q_T}{T} = \frac{1}{T}\nu RT \ln\frac{V_2}{V_1} = \nu R \ln\frac{V_2}{V_1}$

熵变计算

已知V&T $\quad S_B - S_A = \nu C_{V,m} \ln\frac{T_B}{T_A} + \nu R \ln\frac{V_B}{V_A}$

已知P&T $\quad S_B - S_A = \nu C_{p,m} \ln\frac{T_B}{T_A} - \nu R \ln\frac{P_B}{P_A}$

已知P&V $\quad S_B - S_A = \nu C_{p,m} \ln\frac{V_B}{V_A} + \nu C_{V,m} \ln\frac{P_B}{P_A}$