广延量(摩尔数|体积|内能|熵)-与总质量成正比

强度量(压强|密度|温度)-与总质量无关

态函数(内能|焓|熵)-描述系统状态参量的函数,非过程量

过程量(功|热)-与初末状态和中间状态有关

理想气体:$pV=\nu RT, U=U(T)$.

第一章 温度+状态方程

1 分子数密度$n=\frac{N}{V}=\frac{\nu N_A}{V}=\frac{mN_A}{\mu V}=\frac{\rho N_A}{\mu}$

2 分子能够靠近的最近距离d称为分子的有效直径.

3 碰壁数 $\Gamma\approx\frac{n\bar{v}}{6}$ 单位时间内碰撞单位器壁面积的分子

$$p=\Gamma I\approx\frac{n\bar{v}}{6}\cdot 2m\bar{v}=\frac{nm\bar{v}^2}{3}$$

$$\bar{v}\approx\left(\frac{3p}{nm}\right)^{1/2}=\left(\frac{3p}{\rho}\right)^{1/2}=\left(\frac{3V_0p}{\mu}\right)^{1/2}$$

$$\Gamma\approx\frac{1}{6}n\bar{v}\approx\frac{1}{6}N_A\left(\frac{3p}{\mu V_0}\right)^{1/2}\quad V_0=22.41\times10^{-3}m^3$$

4 碰撞频率(单个分子在单位时间内与其他分子的平均碰撞次数)单个动$Z=\frac{N\sigma\bar{v}\Delta t}{\Delta t}=n\bar{v}\pi d^2$,又平均相对速率$\bar{u}=\sqrt{2}\bar{v}$,

碰撞频率$Z=\sqrt{2}\pi d^2n\bar{v}=\sqrt{2}\pi d^2N_A\left(\frac{3p}{\mu V_0}\right)^{1/2}$,

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

5 准静态-无限缓慢-中间态可看作平衡态-无数个平衡态

6 理想气体,足够稀薄,严格满足$pV=\nu RT=NkT, k=\frac{R}{N_A}$.

7 道尔顿$p=\Sigma_{i=1}^n p_i, p_iV=\frac{m_i}{\mu_i}RT, pV=\frac{M}{\bar{\mu}}RT$

8 范德瓦尔斯 $\left(p+\frac{\nu^2a}{V^2}\right)(V-\nu b)=\nu RT$,对 p 分子间作用力修正,对 V 固有体积修正

9 平衡态$V=V(p,T), \mathrm{d}V=\left(\frac{\partial V}{\partial T}\right)_p\mathrm{d}T+\left(\frac{\partial V}{\partial p}\right)_T\mathrm{d}p$

等压体膨胀系数$\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$,等温体膨胀系数$\beta=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$,

$\mathrm{d}V=\alpha V\mathrm{d}T-\beta V\mathrm{d}p, V=V_0[1+\alpha(T-T_0)-\beta(p-p_0)]$.

*利用α,β推导状态方程

第二章 热力学第一定律

1 做功改变系统内能-外界有规则运动能量和系统分子无规则热运动能量的转化和传递(无体积变化可做功-电磁等)

2 焦耳热功当量实验-否定热质说，建立热功换算关系

3 热容量$C=\frac{\text{đ}Q}{\mathrm{d}T}, C_V=\left(\frac{\text{đ}Q}{\mathrm{d}T}\right)_V, C_p=\left(\frac{\text{đ}Q}{\mathrm{d}T}\right)_p$

4 热一$\Delta U=Q+W$，能量守恒在热宏观过程中的具体表述

$$\oint\mathrm{d}U=\oint\text{đ}W+\oint\text{đ}Q,\text{第一类永动机不可能.}$$

孤立系统$Q=W=0\Rightarrow\Delta U=0$,孤立系统内能不变.

5 无限小的准静态过程,外界对系统做功$\text{đ}W=-p\mathrm{d}V$,等容过程$\text{đ}Q=\mathrm{d}U$,等容过程吸收热量等于系统内能增量;等压过程$\mathrm{d}p=0, \text{đ}Q=\mathrm{d}U+p\mathrm{d}V=\mathrm{d}(U+pV)$,定义焓$H=U+pV$,等压过程中吸收热量等于系统焓的增量.

定容热容$C_V=\left(\frac{\text{đ}Q}{\mathrm{d}T}\right)_V=\left(\frac{\partial U}{\partial T}\right)_V$,定压热容$C_p=\left(\frac{\text{đ}Q}{\mathrm{d}T}\right)_p=\left(\frac{\partial H}{\partial T}\right)_p$.

6 $\mathrm{d}U=\left(\frac{\partial U}{\partial T}\right)_V\mathrm{d}T+\left(\frac{\partial U}{\partial V}\right)_T\mathrm{d}V$,绝热自由膨胀$W=Q=\mathrm{d}T=0$,理想气体的内能与体积/压强无关,$U=U(T)$,故理想气体内能$U=\int_{T_0}^T C_V\mathrm{d}T+U_0$,焓$H=U(T)+\nu RT=\int_{T_0}^T C_p\mathrm{d}T+H_0$.

故$C_p=\frac{\mathrm{d}H}{\mathrm{d}T}=\frac{\mathrm{d}U}{\mathrm{d}T}+\nu R=C_V+\nu R, C_{p,m}=C_{V,m}+R$(迈耶公式).

7 外界在绝热过程中对系统所做的功转换成了系统的内能.

$\text{đ}Q=\nu C_{V,m}\mathrm{d}T+p\mathrm{d}V=0, p\mathrm{d}V+V\mathrm{d}p=\nu R\mathrm{d}T\Rightarrow$

$\text{đ}Q=\nu C_{p,m}\mathrm{d}T-V\mathrm{d}p=0, \frac{C_{p,m}}{C_{V,m}}\frac{\mathrm{d}V}{V}+\frac{\mathrm{d}p}{p}=0$,热容比$\gamma=\frac{C_{p,m}}{C_{V,m}}\Rightarrow$

$pV^\gamma=C, TV^{\gamma-1}=C, \frac{p^{\gamma-1}}{T^\gamma}=C, \gamma=\gamma(T)$.

功$W=\frac{p_1V_1-p_2V_2}{\gamma-1}=\frac{p_1V_1}{\gamma-1}\left[\left(\frac{V_1}{V_2}\right)^{\gamma-1}-1\right]=\frac{p_1V_1}{\gamma-1}\left[\left(\frac{p_2}{p_1}\right)^{(\gamma-1)/\gamma}-1\right]$.

8 洛夏德实验$pA=p_0A+mg, \mathrm{d}V=Ay, \mathrm{d}p=-\gamma p\frac{\mathrm{d}V}{V}\Rightarrow$

$f=A\mathrm{d}p=-\gamma A^2\frac{p}{V}y, T=2\pi\sqrt{mV/\gamma pA^2}, \gamma=\frac{4\pi^2mV}{A^2pT^2}$.

9 多方过程$pV^n=C$,等压(0),等容(∞),等温(1),绝热(γ).

*热一推导

10 绝热节流-绝热条件下从大压强空间经多孔塞缓慢迁移到小压强空间的过程-焦-汤验证得实际气体内能与体积/压强也有关.绝热节流过程等焓,理想气体温度不变.

11 焦-汤效应-真实气体节流膨胀后温度变化.$\alpha=\left(\frac{\partial T}{\partial p}\right)_H$

$\alpha>0$,制冷区,温降; $\alpha<0$,制热区,温升; $\alpha=0$反转曲线.

反转曲线方程$T=\frac{2a(V-b)^2}{RBV^2}, T_{max}=\frac{2a}{Rb}$.

12 循环过程(回到初始状态),工作物质.$\Delta U=0$,顺正逆逆.

13 热机-从高温热源吸热,对外做功和对低温热源放热循环.效率$\eta=\frac{W}{Q_1}=\frac{Q_1-Q_2}{Q_1}$.理论上效率最高-卡诺热机$\eta=1-\frac{T_2}{T_1}$.

提高效率:升高高温热源温度,降低低温热源温度.

14 制冷机-从低温热源吸热外界对其做功,对高温热源放热.逆向卡诺循环,制冷系数$\varepsilon=\frac{Q_2}{Q_1-Q_2}=\frac{T_2}{T_1-T_2}$.

第三章 热力学第二定律

1 功热转换过程有方向.(开)不能只从单一热源吸热对外做功不产生其他影响;(克)不能把热量从低温物传到高温物不引起外界变化.两者等效.可证绝热线不可相交(引入等温线).

2 卡诺定理不可逆热机效率不大于可逆热机$\eta\le1-\frac{T_2}{T_1}$.对相同高温低温下任意可逆热机,其效率相同,与工作物质无关.

3 利用卡诺热机效率有$\left(\frac{\partial U}{\partial V}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_V-p$

$\mathrm{d}U=\left(\frac{\partial U}{\partial T}\right)_V\mathrm{d}T+\left(\frac{\partial U}{\partial V}\right)_T\mathrm{d}V=C_V\mathrm{d}T+\left[T\left(\frac{\partial p}{\partial T}\right)_V-p\right]\mathrm{d}V\Rightarrow$

$\text{đ}Q=\mathrm{d}U+p\mathrm{d}V=C_V\mathrm{d}T+T\left(\frac{\partial p}{\partial T}\right)_V\mathrm{d}V=\left[C_V+T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p\right]\mathrm{d}T+T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T\mathrm{d}p$

$C_p=\frac{(\text{đ}Q)_p}{(\mathrm{d}T)_p}=C_V+T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p$

4 热温比:等温过程吸热与热源温度之比.克劳修斯等式-可逆循环视作许多可逆卡诺循环$\oint_r\frac{\text{đ}Q}{T}=0$,对任一可逆循环过程,热温比之和为零.克劳修斯不等式-不可逆循环可视为部分或全部由不可逆卡诺循环组成,$\oint_{Ir}\frac{\text{đ}Q}{T}<0$.工作在一对恒温热源之间的热机,各等温过程的热温比之和小于等于零.

5 熵-对于一个可逆循环,$\int_A^B\frac{\text{đ}Q}{T}$只决定于系统初末状态与过程无关-定义态函数$S_B-S_A=\int_A^B\frac{\text{đ}Q}{T}$,绝热过程$\Delta S=0$

6 理想气体 $S=C_V\ln T+\nu R\ln V+C=C_p\ln T-\nu R\ln p+C=C_V\ln p+C_p\ln V+C$; $C_V=\left(\frac{\text{đ}Q}{\mathrm{d}T}\right)_V=\left(\frac{T\mathrm{d}S}{\mathrm{d}T}\right)_V$

7 $T\mathrm{d}S=\mathrm{d}U+p\mathrm{d}V, \mathrm{d}S=\frac{1}{T}\mathrm{d}U+\frac{p}{T}\mathrm{d}V\Rightarrow T=\left(\frac{\partial U}{\partial S}\right)_V$温度-系统体积一定,内能对熵的变化率

8 熵增加原理$S_2-S_1\ge\int_1^2\frac{\text{đ}Q}{T}$,绝热系统内部进行任何过程熵永不减少,孤立系统也是绝热系统,总从非平衡态到平衡态过渡.平衡态-熵值最大.

9 熵的统计解释(玻尔兹曼熵公式)$S=k\ln\Omega$,Ω宏观状态对应的微观状态数.

第四章 麦克斯韦-玻尔兹曼分布律

1 理想气体-略分子线度,完全弹性碰撞,略其余相互作用

2 大量分子统计假设-每个分子位于任意处速度指向任意方向机会相同,$\overline{v_x}=\overline{v_y}=\overline{v_z}=0, \overline{v_x^2}=\overline{v_y^2}=\overline{v_z^2}=\frac{1}{3}\overline{v^2}$.

3 理想气体压强$p=\frac{F}{\Delta S}=\frac{2}{3}n\overline{\varepsilon_k^t}$,$n$为分子数密度,$\overline{\varepsilon_k^t}$是平均平动动能,$p=nkT\Rightarrow\overline{\varepsilon_k^t}=\frac{3}{2}kT$,温度是大量热运动气体分子的平均动能的度量,温度相同的理想气体分子$\overline{\varepsilon_k^t}$相同.

4 概率分布$\mathrm{d}P=\frac{\mathrm{d}N}{N}=\frac{h(x)\mathrm{d}x}{\int h(x)\mathrm{d}x}=f(x)\mathrm{d}x$,$f(x)$概率分布函数归一化$\int f(x)\mathrm{d}x=1$,$\mathrm{d}P=f(x)\mathrm{d}x$随机变量$x$在$x\sim x+\mathrm{d}x$之间的概率,$\bar{x}=\int xf(x)\mathrm{d}x$, $\overline{G(x)}=\int G(x)f(x)\mathrm{d}x$,在$x_1\sim x_2$区间内平均值$\overline{G(x)}'=\int_{x_1}^{x_2}G(x)f(x)\mathrm{d}x\,/\int_{x_1}^{x_2}f(x)\mathrm{d}x$

5 麦克斯韦速度分布律$f(v_x,v_y,v_z)=f(v_x)f(v_y)f(v_z)=f(v_x^2+v_y^2+v_z^2)=f(v^2)$.对$v_x$求偏导,有$\frac{1}{f(v^2)}\frac{\mathrm{d}f(v^2)}{\mathrm{d}v^2}=\frac{1}{f(v_x)}\frac{\mathrm{d}f(v_x)}{\mathrm{d}v_x^2}\Rightarrow f(v_x)=C_0e^{-\beta v_x^2}$,对$v_y,v_z$同理,有$f(v_x,v_y,v_z)=Ce^{-\beta(v_x^2+v_y^2+v_z^2)}$,归一化得$C=\left(\frac{\beta}{\pi}\right)^{3/2}$,利用$\overline{\varepsilon_k^t}$确定了$\beta=\frac{m}{2kT}$.

$f(v_x)=\left(\frac{m}{2\pi kT}\right)^{1/2}e^{-\frac{1}{2}mv_x^2/kT}$,

$f(v_x,v_y,v_z)=\left(\frac{m}{2\pi k}\right)^{3/2}e^{-\frac{1}{2}mv^2/kT}$

6 $f(\vec{v})\mathrm{d}\vec{v}=\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}e^{-\frac{\frac{1}{2}mv^2}{kT}}v^2\sin\theta\,\mathrm{d}v\mathrm{d}\theta\mathrm{d}\varphi$

$f(v)\mathrm{d}v=\left(\frac{m}{2\pi kT}\right)^{3/2}e^{-\frac{1}{2}mv^2/kT}v^2\mathrm{d}v\int_0^\pi\sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\varphi$,

速率分布$f(v)=4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}e^{-\frac{1}{2}mv^2/kT}v^2$.

7 最概然速率$\frac{\mathrm{d}f(v)}{\mathrm{d}v}=0\Rightarrow v_P=\sqrt{\frac{2kT}{m}}=\sqrt{\frac{2RT}{\mu}}$ 速率分布

平均速率$\bar{v}=\int_0^\infty vf(v)\mathrm{d}v=\sqrt{\frac{8kT}{\pi m}}=\sqrt{\frac{8RT}{\pi\mu}}$ 分子碰撞

方均根速率$\sqrt{\overline{v^2}}=\sqrt{\frac{3kT}{m}}=\sqrt{\frac{3RT}{\mu}}$ 平均平动动能

8 分布律→理想气体状态 $\mathrm{d}I=nmv_x^2f(v)\mathrm{d}v\mathrm{d}\sigma$

$\mathrm{d}F=\frac{\mathrm{d}I}{\mathrm{d}t}=\frac{\mathrm{d}(I_{L\to R}+I_{R\to L})}{\mathrm{d}t}=$

$nm\left(\frac{m}{2\pi kT}\right)^{1/2}\mathrm{d}\sigma\int_{-\infty}^\infty v_x^2e^{-\frac{1}{2}mv_x^2/kT}\mathrm{d}v_x\Rightarrow p=\frac{\mathrm{d}F}{\mathrm{d}\sigma}=$

$nm\left(\frac{m}{2\pi kT}\right)^{1/2}2\cdot\frac{1}{4}\sqrt{\frac{\pi}{\left(\frac{m}{2kT}\right)^3}}=nkT\Rightarrow pV=NkT=\nu RT$

9 碰壁数 $\Gamma=\frac{\mathrm{d}N}{\mathrm{d}\sigma}=n\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v_xe^{-\frac{1}{2}mv_x^2/kT}\mathrm{d}v_x\int_{-\infty}^\infty e^{-\frac{1}{2}mv_y^2/kT}\mathrm{d}v_y\int_{-\infty}^\infty e^{-\frac{1}{2}mv_z^2/kT}\mathrm{d}v_z=$

$\frac{1}{4}n\left(\frac{8kT}{\pi m}\right)^{1/2}=\frac{1}{4}n\bar{v}$.小孔泻流-小孔界面线度不大于气体分子平均自由程,单位时间从泻流小孔跑出气体分子数为$\Delta N=\frac{1}{4}n\bar{v}\mathrm{d}\sigma\propto m^{-1/2}$,质量越小越容易逸出容器.

10 玻尔兹曼分子数密度$p(z+\mathrm{d}z)\Delta S+mgn\Delta S\mathrm{d}z=p(z)\Delta S$

$\mathrm{d}p=-mgn\mathrm{d}z, p=nkT\Rightarrow\frac{\mathrm{d}n}{n}=-\frac{mg}{kT}\mathrm{d}z\Rightarrow n(z)=n_0e^{-\frac{mgz}{kT}}$

$p=n(z)kT=p_0e^{-\frac{mgz}{kT}}, z=-\frac{kT}{mg}\ln\frac{p(z)}{p_0}=-\frac{RT}{\mu g}\ln\frac{p(z)}{p_0}$.

从重力场推广有$n=n_0e^{-\varepsilon_p(\vec{r})/kT}$.

11 麦克斯韦(速度空间)玻尔兹曼(位置空间)

$f_{MB}(\vec{r},\vec{v})=\frac{n_0}{N}\left(\frac{m}{2\pi kT}\right)^{3/2}e^{-\frac{\varepsilon}{kT}}=\frac{1}{\iiint_V e^{-\varepsilon_p/kT}\mathrm{d}V}\left(\frac{m}{2\pi k}\right)^{3/2}e^{-\frac{\varepsilon}{kT}}$ 表示处于温度为T的外力场内平衡态理想气体中分子在$\vec{r}$处单位位置空间内且在$\vec{v}$处单位速度空间内出现的概率,$\varepsilon=\varepsilon_p(\vec{r})+\frac{1}{2}m\vec{v}^2$单原子分子总能量，$\varepsilon=\varepsilon_p(\vec{r})+\varepsilon_k(\vec{r},\vec{v})$多原子分子总能量(平动|转动|振动).

12 自由度-理想气体(刚性),$i=3$单,$i=3+2$双,$i=3+3$多.实际(振动)$i=3$单,$i=3+2+1$双,$i=3+3+(3N-6)$多

$i=t+r+s=3N$,平动+转动+振动

13 能量均分原理-温度为T的平衡态,系统中的每个自由度都有相等的平均热运动动能$\frac{1}{2}kT$,平衡态下气体分子各个自由度的热运动平均平动动能相等是分子热运动最无序混乱的一种表现.$\bar{\varepsilon}=\frac{i}{2}kT=\frac{t+r+2s}{2}kT$.

14 理想气体的内能$U=N\bar{\varepsilon}=\frac{t+r+2s}{2}NkT=\frac{t+r+2s}{2}\nu RT$

$C_V=\left(\frac{\partial U}{\partial T}\right)_V=\frac{t+r+2s}{2}\nu R, C_{V,m}=\frac{t+r+2s}{2}R$与温度无关.

在低温下,气体的转动和振动运动不参加热运动;在常温下,平动和转动参加;高温下,平动转动振动都参与热运动.

常用数学

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

2 $\left(\frac{\partial y}{\partial x}\right)_z\left(\frac{\partial x}{\partial y}\right)_z=1, \left(\frac{\partial F}{\partial x}\right)_z=\left(\frac{\partial F}{\partial w}\right)_z\left(\frac{\partial w}{\partial x}\right)_z$

3 $\int_0^\infty e^{-\lambda x^2}\mathrm{d}x=\frac{1}{2}\sqrt{\pi/\lambda}$, $\quad\int_0^\infty xe^{-\lambda x^2}\mathrm{d}x=\frac{1}{2\lambda}$

$\int_0^\infty x^2e^{-\lambda x^2}\mathrm{d}x=\frac{1}{4}\sqrt{\pi/\lambda^3}$, $\quad\int_0^\infty x^3e^{-\lambda x^2}\mathrm{d}x=\frac{1}{2\lambda^2}$

$\int_0^\infty x^4e^{-\lambda x^2}\mathrm{d}x=\frac{3}{8}\sqrt{\pi/\lambda^5}$, $\quad\int_0^\infty x^5e^{-\lambda x^2}\mathrm{d}x=\frac{1}{\lambda^3}$

$\int_0^\infty x^6e^{-\lambda x^2}\mathrm{d}x=\frac{15}{16}\sqrt{\pi/\lambda^7}$, $\quad\int_0^\infty x^7e^{-\lambda x^2}\mathrm{d}x=\frac{3}{\lambda^4}$

例 $U=U(p,V)$.

$đQ=\mathrm{d}U+p\mathrm{d}V=\left(\frac{\partial U}{\partial p}\right)_V\mathrm{d}p+\left(\frac{\partial U}{\partial V}\right)_p\mathrm{d}V+p\mathrm{d}V=\left(\frac{\partial U}{\partial p}\right)_V\mathrm{d}p+[\left(\frac{\partial U}{\partial V}\right)_p+p]\mathrm{d}V$

$\left(\frac{\partial U}{\partial p}\right)_V=\left(\frac{\partial U}{\partial T}\frac{\partial T}{\partial p}\right)_V=-C_V\left(\frac{\partial V}{\partial p}\right)_T/\left(\frac{\partial V}{\partial T}\right)_p=\frac{C_V\beta}{\alpha}$

$\left(\frac{\partial U}{\partial V}\right)_p=\left(\frac{\partial Q-p\partial}{\partial V}\right)_p=\left(\frac{\partial Q}{\partial T}\frac{\partial T}{\partial V}\right)_p-p=\frac{C_p}{V\alpha}-p$

例 $U=U(T,p)$.

$đQ=\mathrm{d}U+p\mathrm{d}V=\left(\frac{\partial U}{\partial T}\right)_p\mathrm{d}T+\left(\frac{\partial U}{\partial p}\right)_T\mathrm{d}p+p\left(\frac{\partial V}{\partial T}\right)_p\mathrm{d}T+p\left(\frac{\partial V}{\partial p}\right)_T\mathrm{d}p$

$C_p=\left(\frac{đQ}{\mathrm{d}T}\right)_p=\left(\frac{\partial H}{\partial T}\right)_p=\left(\frac{\partial U}{\partial T}\right)_p+p\left(\frac{\partial V}{\partial T}\right)_p=\left(\frac{\partial U}{\partial T}\right)_p+pV\alpha$

$C_p-C_V=T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p\Rightarrow\left(\frac{đQ}{\mathrm{d}p}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T=-\left(C_p-C_V\right)\frac{\beta}{\alpha}$,

$\left(\frac{\partial U}{\partial p}\right)_T=\left(\frac{đQ}{\mathrm{d}p}\right)_T-p\left(\frac{\partial V}{\partial p}\right)_T=pV\beta-\left(C_p-C_V\right)\frac{\beta}{\alpha}$.

例 设速度的概率密度函数为$f\left(v_x,v_y,v_z\right)$,因各向同性,速度空间有$f\left(v_x,v_y,v_z\right)=g(v)$,速率概率密度函数$4\pi v^2g(v)$.只考虑 $v_x>0$ 情况的泻流,有 $v=\iiint v\cos\theta\, g(v)v^2\sin\theta\,\mathrm{d}v\mathrm{d}\theta\mathrm{d}\varphi=\pi\int_0^\infty v^3g(v)\mathrm{d}v=\frac{1}{4}\int_0^\infty v4\pi v^2g(v)\mathrm{d}v=\frac{1}{4}\bar{v}$.

例 单位面积单位时间的面元受冲量

$\mathrm{d}I=I_0\mathrm{d}N(v_x)=2mv_x\,nf(v_x)v_x\mathrm{d}v_x\int_{-\infty}^{\infty}f\left(v_y\right)\mathrm{d}v_y\int_{-\infty}^{\infty}f(v_z)\mathrm{d}v_z\,\mathrm{d}A\mathrm{d}t$

$p=\frac{I}{\mathrm{d}A\mathrm{d}t}=\int_0^\infty 2mv_xnf(v_x)v_x\mathrm{d}v_x=nm\overline{v_x^2}=\frac{1}{3}nm\overline{v^2}$.

例 固体等温压缩

$\mathrm{d}V=\left(\frac{\partial V}{\partial p}\right)_T\mathrm{d}p+\left(\frac{\partial V}{\partial T}\right)_p\mathrm{d}T=-\beta V\mathrm{d}p=-\frac{\beta M}{\rho}\mathrm{d}p$,

外界做功$W=-\int_{V_1}^{V_f}p\mathrm{d}V=\int_{p_1}^{p_f}\frac{p\beta M}{\rho}\mathrm{d}p=\frac{\beta M}{2\rho}(p_f^2-p_1^2)$.

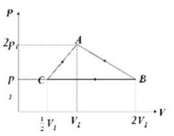
例 $đQ=\nu C_{V,m}\mathrm{d}T+p\mathrm{d}V=\nu C_m\mathrm{d}T,\nu\left(C_m-C_{V,m}\right)\mathrm{d}T=p\mathrm{d}V$

理想气体$p\mathrm{d}V+V\mathrm{d}p=\nu R\mathrm{d}T$,则$\frac{C_m-C_{V,m}}{R}(p\mathrm{d}V+V\mathrm{d}p)=p\mathrm{d}V$

得$\left(C_m-C_{p,m}\right)\frac{\mathrm{d}V}{V}+\left(C_m-C_{V,m}\right)\frac{\mathrm{d}p}{p}=0\Rightarrow pV^n=C$,其中

$n=\frac{C_m-C_{p,m}}{C_m-C_{V,m}}$.

例 1mol多原子分子的理想气体进行循环,求循环效率.



$W=S_{\Delta\mathrm{AB}}=\frac{1}{2}p_1\frac{3}{2}V_1=\frac{3}{4}p_1V_1$

AB: $p=-\frac{p_1}{V_1}V+3p_1$,

$đQ=\nu C_{V,m}\mathrm{d}T+p\mathrm{d}V=4p\mathrm{d}V+3V\mathrm{d}p=\left(12p_1-\frac{7p_1}{V_1}V\right)\mathrm{d}V$,

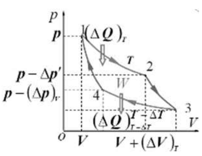
故吸放热转换点为$V_M=\frac{12}{7}V_1$

$Q_{CA}=\Delta U_{CA}+W_{CA}=\nu C_{V,m}\Delta T_{CA}+S_{CA}=\frac{21}{4}p_1V_1$

$Q_{AM}=\int_{\mathrm{V_A}}^{\mathrm{V_M}}\left(12p_1-\frac{7p_1}{V_1}V\right)\mathrm{d}V=\frac{25}{14}p_1V_1$

$\eta=\frac{W}{Q_{CA}+Q_{AM}}=10.66\%$.

例 卡诺循环有$\eta=\frac{W}{Q}=\frac{\Delta T}{T}$,



$W=(\Delta p)_V(\Delta V)_T$,等温过程有$(\Delta Q)_T=(\Delta U)_T+\frac{1}{2}(p+p-\Delta p')(\Delta V)_T$,则

$(\Delta p)_V(\Delta V)_TT=(\Delta U)_T\Delta T+p(\Delta V)_T\Delta T+o(\Delta T\Delta)\Rightarrow$

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

例 理想气体体积膨胀四倍,以下四种过程熵增:

(1)绝热自由膨胀$(\Delta T=0)\Delta S=C_V\ln\frac{T_2}{T_1}+\nu R\ln\frac{V_2}{V_1}=\nu R\ln 4$

(2)可逆等温膨胀$\Delta S=C_V\ln\frac{T_2}{T_1}+\nu R\ln\frac{V_2}{V_1}=\nu R\ln 4$

(3)可逆绝热膨胀$(\mathrm{T}_1V^{\gamma-1}=T_2(4V)^{\gamma-1},\frac{T_2}{T_1}=4^{1-\gamma})$

$\Delta S=C_V\ln\frac{T_2}{T_1}+\nu R\ln\frac{V_2}{V_1}=C_V(1-\gamma)\ln 4-\nu R\ln 4=0$.

(4)绝热节流膨胀$(H=U+pV\Rightarrow p_2=\frac{p_1}{4})$ $\Delta S=C_V\ln\frac{p_2}{p_1}+C_p\ln\frac{V_2}{V_1}=\nu R\ln 4$.

例 由$T\mathrm{d}S=\mathrm{d}U+p\mathrm{d}V$,有$T\left(\frac{\partial S}{\partial T}\right)_p=\left(\frac{\partial U}{\partial T}\right)_p+p\left(\frac{\partial V}{\partial T}\right)_p$

又$\left(\frac{\partial U}{\partial T}\right)_p=\left(\frac{\partial Q}{\partial T}\right)_p-p\left(\frac{\partial V}{\partial T}\right)_p$,得$\left(\frac{\partial S}{\partial T}\right)_p=\frac{C_p}{T}$.

$\left(\frac{\partial S}{\partial V}\right)_p=\left(\frac{\partial S}{\partial T}\right)_p/\left(\frac{\partial V}{\partial T}\right)_p=\left(\frac{C_p}{T}\right)/V\alpha=\frac{C_p}{TV\alpha}$.

例 均匀杆温度一端为T_1,另一端为T_2,计算达到稳定温度$\frac{T_1+T_2}{2}$过程的熵增.

位于$l\sim l+\mathrm{d}l$的小段初温$T_1+\frac{T_2-T_1}{L}l$末温$\frac{T_1+T_2}{2}$

熵增$\mathrm{d}S=\int_T^{T_f}\frac{C\mathrm{d}T}{T}\mathrm{d}l=C\ln\frac{T_1+T_2}{2}/(T_1+\frac{T_2-T_1}{L}l)\,\mathrm{d}l$

熵广延量,则 $\Delta S=\int_0^L\mathrm{d}S=CL\ln\frac{T_1+T_2}{2}-\frac{C}{\frac{T_2-T_1}{L}}\left[\left(T_1+\frac{T_2-T_1}{L}l\right)\ln\left(T_1+\frac{T_2-T_1}{L}l\right)-\left(T_1+\frac{T_2-T_1}{L}l\right)\right]_0^L$

$=CL\ln\frac{T_1+T_2}{2}-\frac{CL}{T_2-T_1}[T_2\ln T_2-T_1\ln T_1-T_2+T_1]$

$=CL[\ln\frac{T_1+T_2}{2}-\frac{T_2\ln T_2-T_1\ln\ _1}{T_2-T_1}+1]$.

例 温度为T的混合理想气体由分子质量为m_1物质的量为C_1的分子和分子质量为m_2物质的量为C_2的分子组成.

其速率分布为

$f(v)=\frac{\mathrm{d}N}{N\mathrm{d}v}=\frac{C_1N_Af_1(v)\mathrm{d}v+C_2N_Af_2(v)\mathrm{d}v}{(C_1+C_2)N_A\mathrm{d}v}=\frac{C_1f_1(v)+C_2f_2(v)}{C_1+C_2}$,

平均速率为

$\bar{v}=\int_0^\infty v\frac{C_1f_1(v)+C_2f_2(v)}{C_1+C_2}\mathrm{d}v=\frac{C_1\overline{v_1}+C_1\overline{v_2}}{C_1+C_2}$

$=\frac{1}{C_1+C_2}\sqrt{\frac{8kT}{\pi}}(\frac{C_1}{\sqrt{m_1}}+\frac{C_2}{\sqrt{m_2}})$.

例 $\left(\frac{n_1}{n_2}\right)_1=\frac{\Gamma_1}{\Gamma_2}=\frac{n_1\overline{v_1}}{n_2\overline{v_2}}=\frac{n_1}{n_2}\left(\frac{m_2}{m_1}\right)^{1/2}$

$\left(\frac{n_1}{n_2}\right)_2=\frac{\Gamma_1}{\Gamma_2}=\left(\frac{n_1}{n_2}\right)_1\frac{\overline{v_1}}{\overline{v_2}}=\frac{n_1}{n_2}\left(\frac{m_2}{m_1}\right)^{2\cdot 1/2}$

$\left(\frac{n_1}{n_2}\right)_N=\frac{\Gamma_1}{\Gamma_2}=\left(\frac{n_1}{n_2}\right)_{N-1}\frac{\overline{v_1}}{\overline{v_2}}=\frac{n_1}{n_2}\left(\frac{m_2}{m_1}\right)^{N\cdot 1/2}$

例 一容器体积$2V$,隔板把它分成相等两半.开始时左边有压强为p_0的理想气体,右边为真空.在隔板上有一面积为S的小孔.求打开小孔后左边气体的压强p随时间t的变化关系.假定过程中左右两边温度相等且保持不变,设分子的平均速率$\bar{v}$.

单位时间左到右$\mathrm{d}N_1=\frac{1}{4}\frac{N}{V}\bar{v}S\mathrm{d}t$右到左$\mathrm{d}N_2=\frac{1}{4}\frac{N_0-N}{V}\bar{v}S\mathrm{d}t$,

净到右的分子数密度$-\mathrm{d}n=\frac{1}{4}\frac{2N-N_0}{V^2}\bar{v}S\mathrm{d}t$,

$\mathrm{d}p=kT\mathrm{d}n=-\frac{1}{4}\frac{2N-N_0}{V^2}kT\bar{v}S\mathrm{d}t=-\frac{1}{4}\frac{2p-p_0}{V}\bar{v}S\mathrm{d}t$,

积分有$\ln\left(p-\frac{p_0}{2}\right)=-\frac{\bar{v}S}{2V}t+C$,则$p=\frac{p_0}{2}\left(e^{-\frac{\bar{v}S}{2V}t}+1\right)$.

例 两个完全相同的物体,热容量都为C,初始温度都为T_i,如果有一个制冷机工作在这两个物体之间,使物体1的温度降低到T_2,另一个物体2的温度升高.至少要对制冷机做多少功?如果功由$\nu\ mol$范德瓦尔斯气体的准静态等温膨胀过程提供,且该过程气体对外所做的功完全提供给制冷机,当气体由V_i膨胀至V_f,该过程中需要保持气体的温度T为多少?范德瓦尔斯气体前后的熵变是多少?

设物体2末温T_3可逆过程总熵变为零,$\int_{T_i}^{T_2}\frac{C\mathrm{d}T}{T}+\int_{T_i}^{T_3}\frac{C\mathrm{d}T}{T}=0$得$T_3=\frac{T_i^2}{T_2}$. $W=C(T_3-T_i)-C(T_i-T_2)=C\left(\frac{T_i^2}{T_2}+T_2-2T_i\right)$.

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

$W=\int_{V_i}^{V_f}p\mathrm{d}V=\int_{V_i}^{V_f}(\frac{\nu RT}{V-\nu b}-\frac{\nu^2a}{V^2})\mathrm{d}V=\nu RT\ln\left(\frac{V_f-\nu b}{V_i-\nu b}\right)+\nu^2a\left(\frac{1}{V_f}-\frac{1}{V_i}\right)\Rightarrow T=\frac{C\left(\frac{T_i^2}{T_2}+T_2-2T_i\right)-\nu^2a\left(\frac{1}{V_f}-\frac{1}{V_i}\right)}{\nu R\ln\left(\frac{V_f-\nu b}{V_i-\nu b}\right)}$.

可逆$\mathrm{d}S=\frac{đQ}{T}=\frac{\mathrm{d}U+p\mathrm{d}V}{T}$,其中$\mathrm{d}U=\left(\frac{\partial U}{\partial V}\right)_T\mathrm{d}V+\left(\frac{\partial U}{\partial T}\right)_V\mathrm{d}T$,

等温$\mathrm{d}U=\left(\frac{\partial U}{\partial V}\right)_T\mathrm{d}V=\left[T\left(\frac{\partial p}{\partial T}\right)_V-p\right]\mathrm{d}V\Rightarrow\mathrm{d}S=\left(\frac{\partial p}{\partial T}\right)_V\mathrm{d}V$

$\mathrm{d}S=\frac{\nu R}{V-\nu b}\mathrm{d}V\Rightarrow\Delta S=\nu R\ln\left(\frac{V_f-\nu b}{V_i-\nu b}\right)$.

例 已知速度分布函数如下,求a,b,v_{x0},v_{y0},v_{z0}.

$f\left(v_x,v_y,v_z\right)=\exp\left\{a-b\left[(v_x-v_{x0})^2+\left(v_y-v_{y0}\right)^2+(v_z-v_{z0})^2\right]\right\}$.

$n=\iiint f\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z=\left(\frac{\pi}{b}\right)^{\frac{3}{2}}e^a$,

$\overline{v_x}=\frac{1}{n}\iiint v_xf\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z=\frac{1}{n}\left(\frac{\pi}{b}\right)^{\frac{3}{2}}v_{x0}e^a$,有 $\overline{v_x}=v_{x0}$,同理 $\overline{v_y}=v_{y0}$, $\overline{v_z}=v_{z0}$.

$\bar{\varepsilon}=\frac{1}{n}\iiint\frac{1}{2}m\left(v_x^2+v_y^2+v_z^2\right)f\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z=\frac{3}{2}kT+\frac{1}{2}m\left(v_x^2+v_y^2+v_z^2\right)$,

代入得$\bar{\varepsilon}=\frac{m}{2n}e^a\left(\frac{\pi}{b}\right)^{\frac{3}{2}}\left[\frac{3}{2b}+\left(v_{x0}^2+v_{y0}^2+v_{z0}^2\right)\right]$,

故$b=\frac{m}{2kT}$, $a=\ln n\left(\frac{m}{2\pi kT}\right)^{3/2}$,得

$f\left(v_x,v_y,v_z\right)=n\left(\frac{m}{2\pi k}\right)^{3/2}\exp\left\{-\frac{m}{2kT}\left[(v_x-\overline{v_x})^2+\left(v_y-\overline{v_y}\right)^2+(v_z-\overline{v_z})^2\right]\right\}$.

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