§17.

热学 $\begin{cases} \text{热力学（宏观，三大定律）} \\ \text{统计物理学（微观）} \end{cases}$

宏观量 $\xleftarrow{\text{统计平均}}$ 微观量.

(可直测)

稳恒态 ≠ 平衡态

↓

（不受外界影响）

温度：共处于平衡态 ⇒ 温度相等

（理想气体 law）

理想气体模型 M一定，T不变：pV为常量，∀P下成立

$pV \propto T$ $\qquad t = T - 273.15$

$pV = \nu RT = \frac{m}{M} RT$ （理想气体状态方程）

$= \frac{N}{N_A} RT$ $\qquad (R = 8.31)$

$\Rightarrow p = nkT$ $\qquad n = \frac{N}{V}$（单位体积分子数）

$pV = \nu RT$ $\begin{cases} T\text{恒定}: pV = c \\ p\text{恒定}: V/T = c \\ V\text{恒定}: p/T = c \end{cases}$

eg. $pV = \frac{m}{M} RT$

$\left.\begin{array}{l} m_1 = \frac{pVM}{RT} \\ m_2 = \frac{p'VM}{RT'} \end{array}\right\} \Rightarrow m_1 - m_2$

$pV = \nu RT$

$(p + dp)S + dmg = pS.$

$\Rightarrow dp = -\rho g\, dh.$ $\qquad pV = \frac{m}{M} RT$

换ρ，换m，积分.

$V = 3.2 \times 10^{-2}.$

$p = 1.3 \times 10^{7}$

$pV = \frac{m}{M} RT$

$m_1 = \frac{MpV}{RT}$

$m_2 = \sim$

平均自由程 $\bar{\lambda}$ （2次碰撞间）

平均碰撞频率 $\bar{z}$ （单位时间）

平均速率 $\bar{v}$

$\Rightarrow \bar{\lambda} = \dfrac{\bar{v}}{\bar{z}}$

$$\bar{\lambda} = \frac{\bar{v}}{\bar{z}} = \frac{1}{\sqrt{2}\,\pi d^2 n}$$

d：分子有效直径　n：单位体积分子数.

$p = nkT$

$$\bar{\lambda} = \frac{kT}{\sqrt{2}\,\pi d^2 p}$$

eg. $p = nkT \Rightarrow n = \dfrac{p}{kT}$

$$\bar{\lambda} = \frac{\bar{v}}{\bar{z}} = \frac{1}{\sqrt{2}\,\pi d^2 n}$$

理想气体压强. ☆ $p = \frac{1}{3} n m \bar{v}^2 = \frac{2}{3} n \bar{\varepsilon}_t$　$\bar{\varepsilon}_t = \frac{1}{2} m \bar{v}^2$ （~~平均动能~~）

$\boxed{\text{平均平动动能}}$

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

$\bar{\varepsilon}_t = \frac{1}{2} m \bar{v}^2$

$\Rightarrow \bar{v} \approx 1.73 \sqrt{\dfrac{RT}{M}}$ （方均根速率）

eg. (1) $p = nkT \Rightarrow n = \dfrac{p}{kT}$

(2). $m = \dfrac{M}{N_A}$

(3) $\bar{\varepsilon}_t = \frac{3}{2} kT$

能量均分定理

自由度
$\begin{cases} ① 单原子\ i=3 \\ ② 刚性双原子\ i=5 \\ ③ 刚性多原子\ i=6 \end{cases}$

☆ $\frac{1}{2}m\bar{v}_x^2 = \frac{1}{2}m\bar{v}_y^2 = \frac{1}{2}m\bar{v}_z^2 = \frac{1}{2}kT$

$\boxed{平均动能}$

$\bar{\varepsilon}_k = \frac{i}{2}kT$

T平衡下，每自由度平均动能都相等且为 $\frac{1}{2}kT$

理想气体内能，$E = \frac{i}{2}\nu RT$

△ 只与T有关

eg. O_2. $i=5$.

$\bar{\varepsilon}_t = \frac{3}{2}kT$ $\quad$ $\bar{\varepsilon}_t \neq \bar{\varepsilon}_k$ $\quad$ $\begin{cases} E = \frac{i}{2}\nu RT \\ \varepsilon = \frac{i}{2}kT \end{cases}$

$\bar{\varepsilon}_k = \frac{5}{2}kT$

$E_k = \frac{5}{2}\nu RT$ $\quad$ $\boxed{\nu = \frac{m}{M}}$ $\quad$ $\begin{cases} p = nkT \\ pV = \frac{m}{M}RT \end{cases}$

(1). ~~$p = nkT$~~

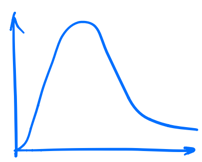
$pV = \nu RT = \frac{m}{M}RT \Rightarrow p\rho = \frac{RT}{M}$ $\quad$ $M = \frac{RT}{p\rho}$

(2). $\bar{\varepsilon}_t = \frac{3}{2}kT$ $\quad$ $\bar{\varepsilon}_k = \frac{5}{2}kT$ $\Rightarrow$ $\bar{\varepsilon}_r = \frac{2}{2}kT$

(3). $E = \frac{5}{2}\frac{N}{N_A}RT$

麦克斯韦速率分布律（分子按速率分布是有规律的）

$f(v) = \frac{dN_v}{N \cdot dv}$

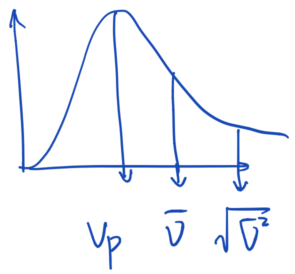


(百分比) 概率密度

(最概然速率) $v_p = \sqrt{\frac{2kT}{m}} \approx 1.41\sqrt{\frac{RT}{M}}$

(平均速率) $\bar{v} = 1.6\sqrt{\frac{RT}{M}}$

$v_p = 1.41\sqrt{\frac{RT}{M}}$ $\qquad$ $\bar{v} = 1.6\sqrt{\frac{RT}{M}}$ $\qquad$ $\sqrt{\bar{v}^2} = 1.73\sqrt{\frac{RT}{M}}$



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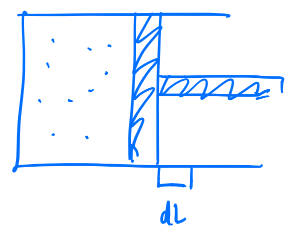
§1.8 内能：系统内所有粒子能量和. $E = E(T, V)$

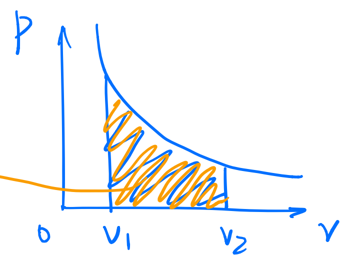
$$\left.\begin{array}{l} \text{做功 } (A) \\ \text{热传递 } (Q) \end{array}\right\} \Rightarrow E(T, V)$$

准静态过程 $\qquad dA = p\,dV$

(体积功、通用)



$\Rightarrow$ $A = \int_{V_1}^{V_2} p\,dV$



热力学定律1. $\quad Q = \Delta E + A$

Q是变化量

$$\begin{cases} Q > 0 & \text{：吸热} \\ \Delta E > 0 & \text{：内能}\uparrow \\ A > 0 & \text{：对外界做功} \end{cases}$$

(适用任何过程)

$+\boxed{\text{准静态}}$: $Q = \Delta E + \int_{V_1}^{V_2} p\,dV$

$+\boxed{\text{理想气体}}$: $Q = \int_{T_1}^{T_2} \underline{\underline{\frac{i}{2}\nu R\,dT}} + A$

$\Rightarrow Q = \int_{T_1}^{T_2} \frac{i}{2}\nu R\,dT + \int_{V_1}^{V_2} p\,dV$

热容： $C = \frac{dQ}{dT} = mc = \nu C_m$ （mol热容）

★ $C_{V,m} = \frac{i}{2} R$ （mol定体）

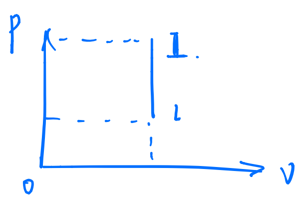
$\Delta E = \nu C_{V,m} \Delta T$ （理想气体通用）

★ $C_{p,m} = \frac{i}{2} R + R$ （mol定压）

$= C_{V,m} + R$

$\gamma = \frac{C_p}{C_V} = \frac{C_{p,m}}{C_{V,m}} = \frac{i+2}{i}$

等体过程. V恒定　$pV = \nu RT$　$\frac{p_1}{p_2} = \frac{T_1}{T_2}$



$A = 0$

$\Delta E = \nu C_{V,m} \Delta T = \frac{i}{2} \nu R \Delta T$ （内能变化通用）

$Q = \Delta E + A = \Delta E = \nu C_{V,m} \Delta T$

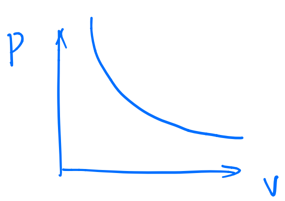
等压： $Q = p(V_2 - V_1) + \Delta E = \nu C_{p,m} \Delta T$ ★

eg. $A = p(V_2 - V_1) = \nu R \Delta T$　$C_{V,m} = \frac{5}{2} R$　$\Delta E = \nu C_{V,m} \Delta T$

p恒定: $\frac{V_1}{V_2} = \frac{T_1}{T_2} \Rightarrow V = RT$　$Q = \Delta E + A$

$p\cancel{V} = \nu RT$

等温　$p_1 V_1 = p_2 V_2$



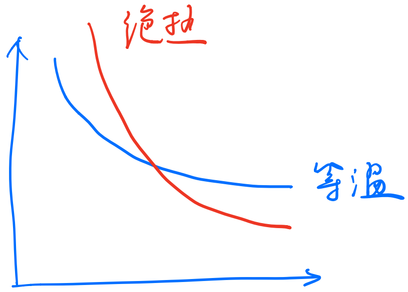
$A = \int_{V_1}^{V_2} p\,dV = p_1 V_1 \ln \frac{p_1}{p_2}$

$\Delta E = 0$

Summary: $\begin{cases} A = \int_{V_1}^{V_2} p\,dT \\ \Delta E = \nu C_{V,m} \Delta T \end{cases}$ $\qquad Q = \Delta E + A.$ $\qquad pV = \nu RT$

$dE = \nu C_{V,m}\, dT$

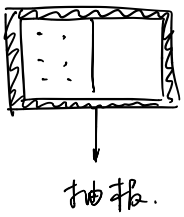
绝热过程: $Q = 0.$



$$\begin{cases} pV^{\gamma} = C_1 \\ TV^{\gamma-1} = C_2 \\ p^{\gamma-1}T^{-\gamma} = C_3 \end{cases}$$ 泊松方程

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

eg.



$Q = 0,\ A = 0 \Rightarrow \Delta E = 0 \Rightarrow T$ 不变

$\boxed{绝热}$

(1).

72L

54L 18L

初态: $p_{10}V_0 = \nu RT_0$

压后: $p_1 = \frac{\nu RT_1}{V_1} = \frac{\nu RT_0}{V_2}$

§19. 熵：$S \propto \ln \Omega$

$S = k \ln \Omega$ 玻耳兹曼熵公式

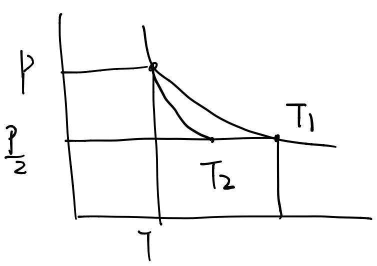
- 熵相加
- 概率相乘

可逆过程，外界条件改变一无穷小量则过程可以反向进行

- 绝热压缩与膨胀
- 等温热传导（温差无限小

$\boxed{\text{孤立系统可逆过程熵不变}}$

eg.

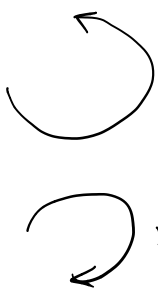


等温膨胀要吸热？

$$Q = \Delta E + A$$

$\Delta E > 0$　$A < 0$

$T_1 - T_2 > 0.$



放热

吸热

与绝热过程相比.

克劳修斯熵公式

$$\begin{cases} dS = \dfrac{dQ}{T} & (\forall\text{系统，可逆过程}) \\ \Delta S = S_1 - S_2 = \displaystyle\int_{1\,(R)}^{2} \frac{dQ}{dT} & (\forall\text{系统，有限可逆}) \end{cases}$$

孤立+可逆
$\forall$ + 可逆绝热 $\Big\} \Rightarrow \Delta S = 0$

$$dS \geqslant \frac{dE + pdV}{T} \quad (\text{可逆取等})$$

Q

$C = \frac{Q}{T} \Rightarrow Q = CT$

$\frac{đQ}{dT} \neq \frac{dQ}{dT}$ ← 单位的

↓ 热容 C_m　　↓ 比热 c

eg. $\Delta S_{水} = \int \frac{đQ}{T} = \int \frac{cm\,dT}{T} = cm \ln \frac{T_2}{T_1}$

$\Delta S_{炉} = \int \frac{đQ}{T} = \frac{1}{T_2} \int đQ = \frac{Q_{炉}}{T_2} = -\frac{Q_{水}}{T_2}$

$1 \to 2 \to 3.$ $\Delta S = (S_3 - S_2) + (S_2 - S_1)$

$= \int_1^2 \frac{đQ}{T} \quad = (C_{p,m} - C_{v,m}) \ln \frac{V_2}{V_1}$

$\int \frac{C_{pm}\, dT}{T} + \int \frac{C_{T,m}\, dT}{T}.$

A　　$pV = \nu RT$　　$\boxed{A = \int p\, dV}$

$\int_{20}^{40} \frac{1}{V} \nu RT\, dV$

$1 \to 3$ $\Delta S = \frac{1}{T} Q = \frac{1}{T} (\nu R T_1 \ln \frac{V_3}{V_1})$

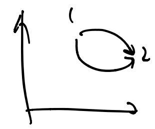
$1 \to 4 \to 1.$ $\Delta S = (S_4 - S_1) + (S_3 - S_4) = \int \frac{C_{p,m}\, dT}{T} = C_{p,m} \ln \frac{T_3}{T_4}$

$\cancel{\frac{T_1}{T_4}} = \frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{\frac{\gamma-1}{\gamma}}$

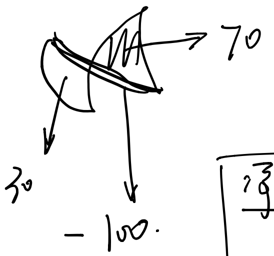
☆

设计为T恒定过程.

$\nu = \frac{m}{M}$



$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dQ}{T} = \int_1^2 \frac{p\,dV}{T} = \nu R \ln\frac{V_2}{V_1}$$



$Q = \Delta E + A \rightarrow$ 净功

净功: 40
吸 100

$pV = \nu RT$

$1 \rightarrow 2.$ $\Delta E = C_{V,m} T_1$

$A = \frac{1}{2}(p_1 + p_2)(V_2 - V_1)$

$= \frac{1}{2} RT_1$

$Q = A + \Delta E$

$2 \rightarrow 3.$ $Q = 0,$ $\Delta E = C_{V,m} \sim$

$3 \rightarrow 1.$ $\Delta E = 0.$ $A = \nu RT_1 \ln\frac{V_1}{V_3}.$

正 loop $= \int_{V_3}^{V_1} p\,dV = RT_1 \ln\frac{1}{8}$

$\eta = 1 - \left|\frac{Q_3}{Q}\right| = -$