Several points:

1714年，华氏温标 ^0F

热学走向实验科学

热质说：希腊火元素学说的进一步发展

但是，不能解释摩擦生热。

相对立的学说：热是一种运动的表现形式

Francis Bacon (1561-1626)

强调理论必须根据实验事实，

热是一种运动

Ломоносов, 1711-1765

热是分子运动的表现，运动守恒

Count Rumford, 1753-1814

制造枪炮切下碎屑温度高，高温碎屑不断产生，

就非是一种运动不可。 (1798)

Humphry Davy, 1778-1829, Chemist

两块冰相互摩擦，完全融化

热功当量：

德国医生 Julius Robert Mayer, 1814-1878

能量守恒，热是能量的一种形式，可与机械能相互转化。

直接实验证据：

James Prescott Joule, 1818-1889

从1840起，用电的热效应

1842年起，机械生热法，

1850年，得到科学界公认，能量守恒

一 热力学第一定律

准静态过程：

在过程进行之中的每一步，物体都处在平衡态

——理想、无摩擦、无限慢、可逆过程

可逆过程：相反方向进行，不在外界引起变化

资本家，"永动机"

1775，巴黎科学院宣布了不接受关于永动机的发明。

绝热过程：状态改变完全是由于机械的或电的直接作用的结果。（沙潭）

(not) (through)

adiabatic : During the change of state, no addition or removal of heat takes place; that is, the system is isolated by adiabatic walls (walls which do not conduct heat) ($\delta Q = 0$)

热质说 → 热量 → C (比热容)

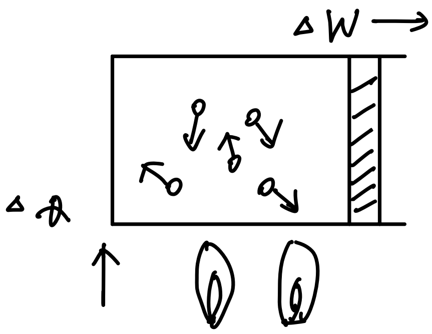
$C(T)$: temperature dependent

1卡 : 15°卡

一克纯水在一个大气压下 14.5°C → 15.5°C 所需热量

1 Calorie ≈ 4.2 Joule

internal energy: 内动能 + 内势能



$$\Delta Q = \Delta U + \Delta W$$

$$\Delta U = \Delta Q - \Delta W$$

$$\Delta E_{in} = \Delta W_{ex}$$

$$\Delta U = \Delta W_{micro} + \Delta W_{macro}$$

$$= \Delta Q - \Delta W$$ (here, 对外做功)

$\boxed{Q: \text{ mysterious energy}}$

W_{micro} is due to molecular collisions at microscopic length scale without changes in macroscopic variables.

计算容易度: $\Delta W > \Delta U > \Delta Q$

ΔQ 作为已知条件

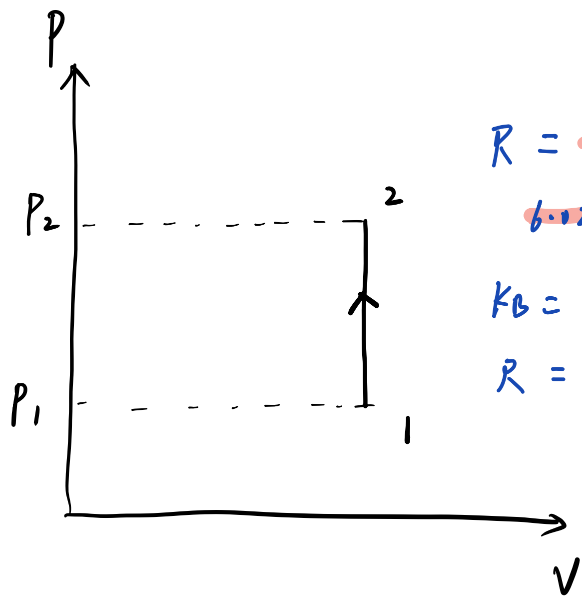
或 $\Delta U + \Delta W$

Calculation :

1° 等容

isochore

/'ai səukɔ:/



$R = N_A k_B$

6.02×10^{23}

$k_B = 1.38 \times 10^{-23}\ J/K$

$R = 8.31\ J/(mol \cdot K)$

$$\Delta W = \int p\, dV = 0$$

\# of degree of freedom

$$\Delta Q = \Delta U = \frac{i}{2} nR(T_2 - T_1)$$

摩尔数

$$= \frac{i}{2}(P_2V_2 - P_1V_1) = \frac{i}{2}(P_2 - P_1)V$$

\# of moles

$$= C_v n \Delta T \quad \left(C_v = \frac{i}{2}R\right)$$

$$\lim_{\Delta T \to 0} \frac{1}{n} \frac{\Delta Q}{\Delta T} = C_v(T)$$ 摩尔等容热容

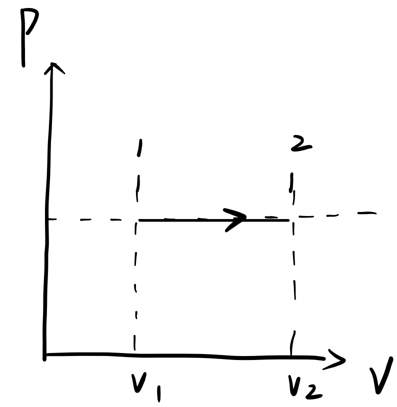
$$\Delta Q = \Delta W + \Delta U = C_v n \Delta T$$

参考书中 C_v 有时指等容热容, $\Delta Q = C_v \Delta T$

II. 等压：

isobaric

/ˌaisəuˈbærik/



$V_2 = 2V_1$

$$\Delta W = F\Delta l = pS\Delta l = p\Delta V$$

$$\Delta W = \int_1^2 p\,dv = p(v_2 - v_1)$$

对于理想气体，内能就是内动能

$$U = \frac{i}{2} nRT \quad \text{(能量按自由度均分)}$$

$$\Delta U = \frac{i}{2} nR(T_2 - T_1) = \frac{i}{2} nR(T_2 - T_1)$$

$$\downarrow \quad p_1V_1 = nRT_1 \qquad p_2V_2 = nRT_2$$

$$= \frac{i}{2} p(V_2 - V_1) \qquad (P_1 = P_2 = P)$$

$$\Delta Q = \Delta U + \Delta W$$

摩尔定压热容

$$= \frac{i+2}{2} p(V_2 - V_1) \qquad C_p = \frac{\Delta Q}{\Delta T}\frac{1}{n}$$

$$= \frac{i+2}{2} nR\Delta T \qquad C_p = (\frac{i}{2}+1)R = C_V + R$$

heat capacity

$$\begin{cases} C_V \equiv \dfrac{1}{n}\left(\dfrac{dQ}{dT}\right)_V & \text{摩尔等容热容} \\[2em] C_p \equiv \dfrac{1}{n}\left(\dfrac{dQ}{dT}\right)_p & \text{摩尔等压热容} \end{cases}$$

$H = U + pV$ (enthalpy: /'enθælpi/)

焓 由荷兰物理学家昂内斯于1909年引入，希腊语: warm within

$$\Delta Q = \Delta U + \Delta W$$

$$dQ = dU + dW$$

seriously, $\bar{d}Q = dU + \bar{d}W$ ($\bar{d}$: 过程相关)

(the differential form of 1st law)

$$\begin{cases} C_V = \dfrac{1}{n}\left(\dfrac{dU}{dT}\right)_V & \text{(体积不变, } dQ = dU\text{)} \\ C_p = \dfrac{1}{n}\left(\dfrac{dH}{dT}\right)_p \end{cases}$$

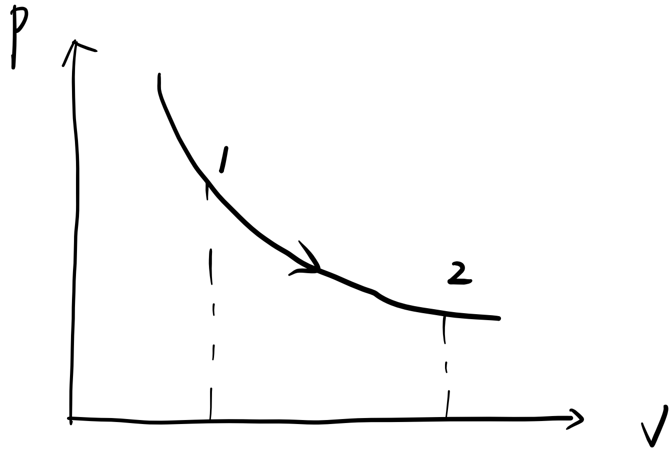
$\because$ $dQ = dU + p\,dV = d(U+pV) - V\,dp$

(等压为0)

$= d(U+pV) = dH$

$$dQ = dU + pdV \xrightarrow{\text{等压}} dU + d(pV)$$
$$= \frac{i}{2} nR\,dT + nR\,dT$$
$$= \left(\frac{i}{2}+1\right) nR\,dT$$
$$C_p = C_v + R$$

Ⅲ° isothermal process



$$\Delta W = \int_1^2 p\,dV$$
$$= \int_1^2 \frac{nRT}{V}\,dV$$
$$= nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta U = 0$$

$$\Delta Q = \Delta U + \Delta W = nRT \ln\left(\frac{V_2}{V_1}\right)$$

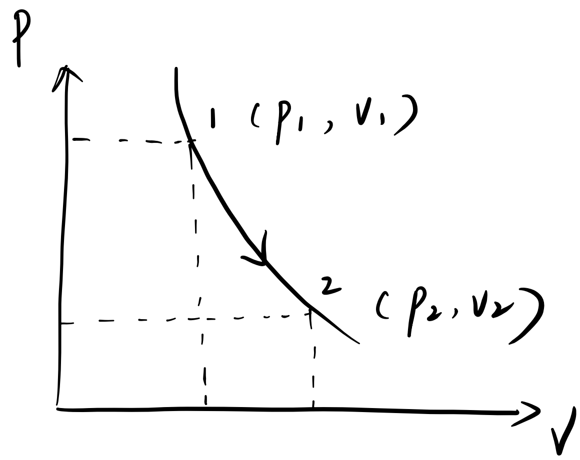
IV adiabatic process

$$\Delta Q = \Delta U + \Delta W = 0 \quad (绝热)$$

（绝热材料 +

抽真空

（失去热交换对象））



$$\Delta U = \frac{i}{2} nR (T_2 - T_1) = \int_{T_1}^{T_2} n C_V \, dT$$

$$= \frac{i}{2} (p_2 V_2 - p_1 V_1) = \frac{i}{2} \Delta (pV)$$

$$\Delta Q = \frac{i}{2} nR \, dT + p \, dV = 0$$

$$\frac{i}{2} (p \, dV + V dp) + p \, dV = 0$$

$$\gamma = \frac{i+2}{i} = \frac{C_p}{C_V}$$

$$\frac{i+2}{2} p \, dV = -\frac{i}{2} V dp$$

$$\gamma \, p \, dV = - V dp$$

$$\gamma \frac{dV}{V} = - \frac{dp}{p} \qquad (*)$$

$$\gamma\, d\ln v = -d\ln p + c$$

$$\gamma \int_{(p_1, v_1)}^{(p_2, v_2)} d\ln v = -\int_{(p_1, v_1)}^{(p_2, v_2)} d\ln p + c_1$$

$$\gamma \ln \frac{v_2}{v_1} = -\ln \frac{p_2}{p_1} + c_1$$

$$\left(\frac{v_2}{v_1}\right)^{\gamma} = c_2 \frac{p_1}{p_2}$$

$$p_1 v_1^{\gamma} = p_2 v_2^{\gamma} = \text{const}$$

---

directly start from (*)

$$\gamma p\, dv + v\, dp = 0$$

$$\gamma \frac{dv}{v} + \frac{dp}{p} = 0 \Rightarrow \gamma\, d\ln v + d\ln p = 0$$

$$\gamma \ln v + \ln p = c \longrightarrow p v^{\gamma} = \text{const}$$

Calculate ΔU, ΔW :

$$\Delta U = \frac{i}{2} nR \, (T_2 - T_1)$$

$$= n C_v \, (T_2 - T_1)$$

$$= \frac{nR}{\gamma - 1} \, (T_2 - T_1)$$

$\downarrow$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{i}{2} + 1}{\frac{i}{2}}$$

$$\frac{\gamma - 1}{1} = \frac{C_p - C_v}{C_v} = \frac{\frac{i}{2} + 1 - \frac{i}{2}}{\frac{i}{2}}$$

$$= \frac{R}{C_v} \Rightarrow$$

$$C_v = \frac{R}{\gamma - 1}$$

$$\Delta W = \int p \, dV \qquad (pV^{\gamma} = C)$$

$$= \int \frac{C}{V^{\gamma}} \, dV$$

$$= c \left. \frac{V^{-\gamma+1}}{-\gamma+1} \right|_1^2$$

$$= c \frac{V_2^{1-\gamma} - V_1^{1-\gamma}}{1-\gamma}$$

$$\downarrow \quad pV^{\gamma} = c$$

$$pV = nRT$$

$$V^{\gamma-1} = \frac{c}{nRT}$$

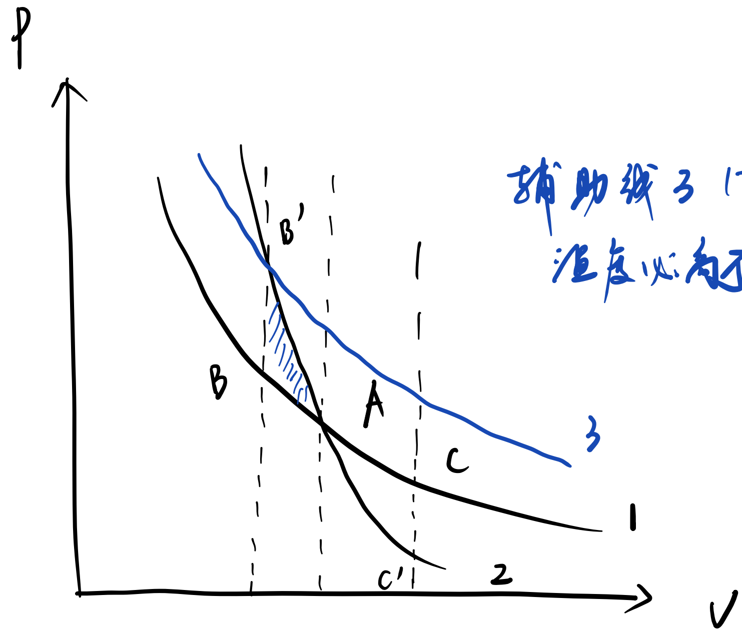
$$= \frac{c\left[\frac{nRT_2}{c} - \frac{nRT_1}{c}\right]}{1-\gamma}$$

$$= \frac{nR}{1-\gamma}(T_2 - T_1) = -\Delta U$$

$\Delta Q = \Delta U + \Delta W = 0$ （绝热）

Isothermal vs adiabatic

绝热过程2
膨胀对外做功
但绝热，那么
只能减小内能
降温。



辅助线3（等温）
温度必高于等温线1

Which one is isothermal?

$$\Delta Q = \Delta U + \Delta W$$

$$\left\{\begin{array}{l} B' \to A \\ B \to A \end{array}\right.$$

$T_{B'} > T_B$

$(pV = nRT)$

绝热：$\Delta U + \Delta W = 0$

对外做功通过降低内能实现

$$\begin{cases} A \to C \\ A \to C' \end{cases} \quad T_C > T_{C'}$$

膨胀对外做功

以降内能，$T\downarrow$

$T_{C'} < T_C$

绝热：$dQ = dU + pdV = 0$

$$U_{C'} < U_C$$

$$pV = c_1 \implies p = c_1/V$$

$$pV^\gamma = c_2 \qquad p = c_2/V^\gamma$$

$\implies V^{\gamma-1} = \dfrac{c_2}{c_1}$

① $\dfrac{\partial p}{\partial V} = c_1 (-1) V^{-2}$

② $\dfrac{\partial p}{\partial V} = c_2 (-\gamma) V^{(-\gamma-1)}$

$$① / ② = \frac{c_1}{c_2} \frac{1}{\gamma} \cancel{V^{\gamma-1}} \left(= \cancel{\frac{c_2}{c_1}}\right)$$

$$= \frac{1}{\gamma}$$

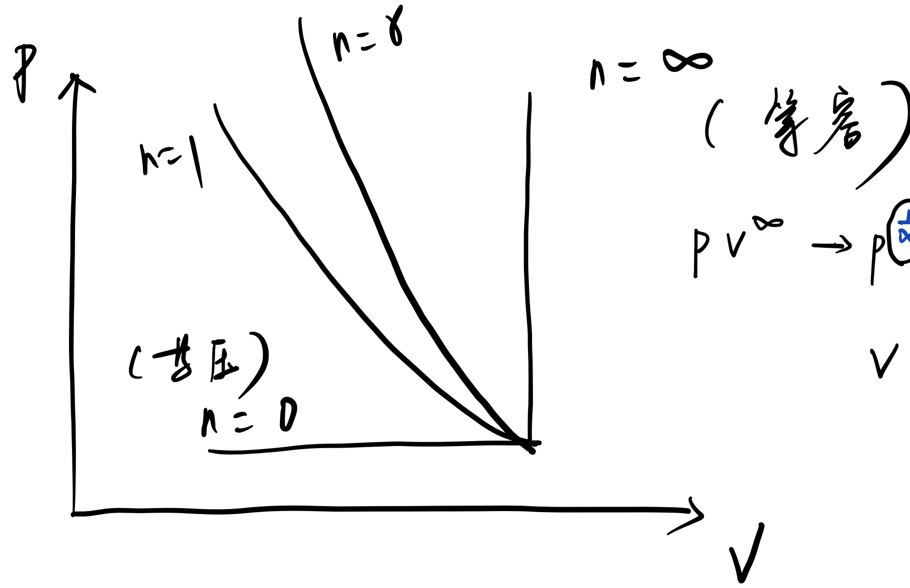
同为负数

$$\left|\frac{\partial p}{\partial V}\right|_① < \left|\frac{\partial p}{\partial V}\right|_②$$

绝热更陡峭

多方过程 (polytropic process)

$$pV^n = \text{const}$$



$$pV^{\infty} \to p^{\frac{1}{\infty}}V, \quad \frac{1}{\infty} \to 0$$

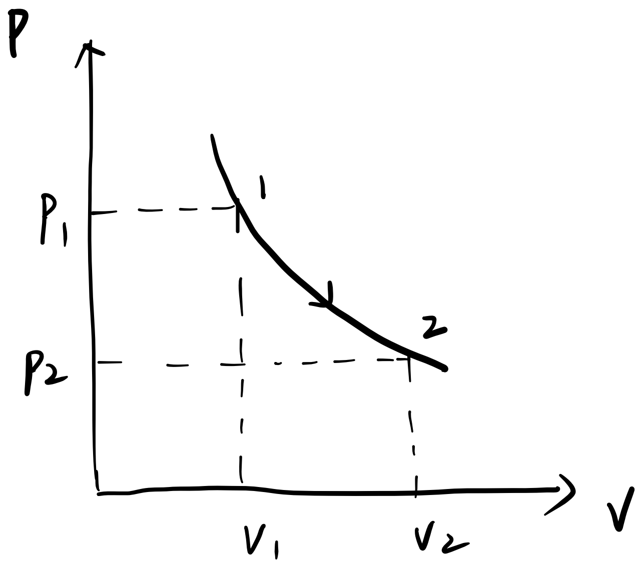
$$\Downarrow$$

$$V = \text{const}$$

$n \in (1, \gamma)$

实际过程

$$dW = p\,dV$$



$$dQ = dU + dW$$

$$\Delta W = \int_1^2 p\,dV$$

$$= \int_1^2 \frac{C}{V^n}\,dV = \left.\frac{V^{1-n}}{1-n}\right|_{V_1}^{V_2}$$

$$= C\,\frac{V_2^{1-n} - V_1^{1-n}}{1-n}$$

$$dU = \frac{i}{2} nR\,dT = \frac{i}{2} d(pV)$$

$$\Delta U = \frac{i}{2}(p_2V_2 - p_1V_1)$$

$$= \frac{i}{2} \left(\frac{c}{V_2^{n-1}} - \frac{c}{V_1^{n-1}} \right)$$

$$= \frac{i}{2} c \left(V_2^{1-n} - V_1^{1-n} \right)$$

$$\Delta W = \frac{1}{1-n} c \left(V_2^{1-n} - V_1^{1-n} \right)$$

$$\Delta U = \frac{i}{2} c \left(V_2^{1-n} - V_1^{1-n} \right)$$

$$\Delta Q = \left(\frac{i}{2} + \frac{1}{1-n} \right) c \left(V_2^{1-n} - V_1^{1-n} \right)$$

$$\xrightarrow{n=\gamma} \frac{1}{1-\gamma} = \frac{1}{1-\frac{c_p}{c_V}} = \frac{c_V}{c_V - c_p}$$

$$\frac{c_V}{c_V - c_p} = \frac{i}{-2}$$

$$\Uparrow$$

$$\frac{c_V}{c_p} = \frac{i}{i+2}$$

多方 → 绝热

$$\gamma = \frac{C_p}{C_v} = \frac{i+2}{2} = \frac{5}{3}$$ （单原子分子）$i=3$

$\gamma = \frac{7}{5}$ （刚性双原子分子） $i=5$

$\gamma = \frac{4}{3}$ （刚性多原子分子（非共线）） $i=6$

（C_p：体积膨胀，做功，吸更多的热）

C_p：保持压强不变

C_v：保持体积不变