Several points:

1714年，华氏温标

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结果。（孙洋）

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

$C(T)$

标准温度 15° 卡

一克纯水在一个大气压下 14.5°C → 15.5°C

所需热量

internal energy: 内动能 + 内势能

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

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

$$= Q - W$$ (here, 对外做功)

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

$$\Delta U = Q - W$$

$$Q = \Delta U + W$$

计算角度: W, ΔU, Q.

Q 直接给

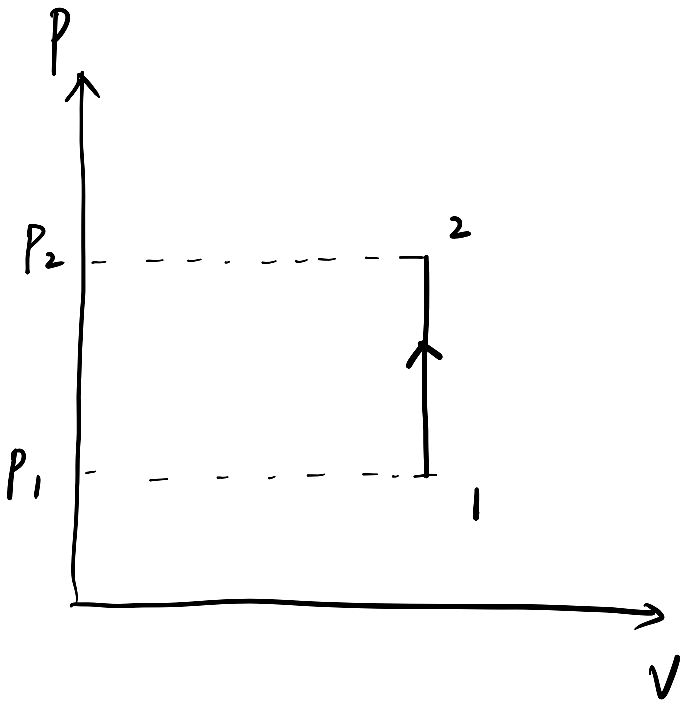
或 $\Delta U + W$

Calculation :

I° 等容

isochore

/ˈaisəukɔːl/



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

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

$$= \frac{i}{2}(p_2V_2 - p_1V_1) = \frac{i}{2}(p_2 - p_1)V$$

$$= C_v n \Delta T$$

$$\boxed{\frac{1}{n}\frac{\Delta U}{\Delta T} = C_v}$$

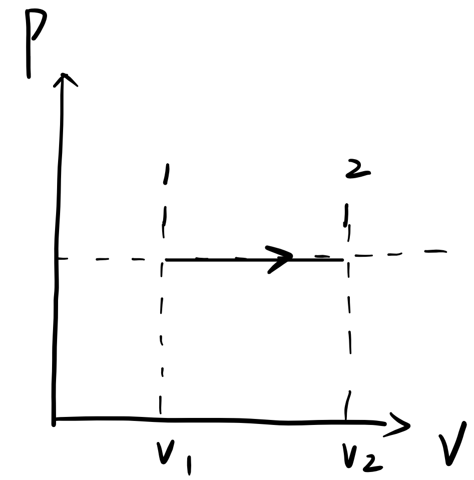
摩尔等容热容

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

Ⅱ. 等压:

isobaric

/ˌaɪsəʊˈbærɪk/



$V_2 = 2V_1$

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

$$\Delta W = \int_1^2 p\, dV = p(V_2 - V_1)$$

对于理想气体，内能就是内动能

$$U = \frac{i}{2} nRT$$

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

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

$$= \frac{i}{2} p(V_2 - V_1)$$

摩尔定压热容

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

$$= \frac{i+2}{2} p(V_2 - V_1)$$

$$= \frac{i+2}{2} nR\Delta T$$

$$\frac{\Delta Q}{\Delta T} = \boxed{C_p}\, nR$$

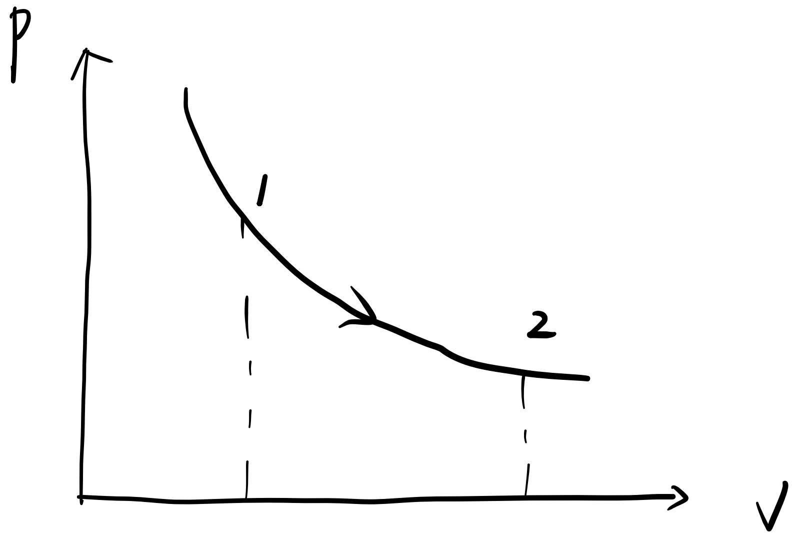
$$C_p = C_v + 1$$

Shankar's trick : $\Delta Q = \Delta U + \Delta W$

$= \Delta U + P \Delta V$

$= \Delta U + \underbrace{\Delta (PV)}_{nR\Delta T}$

VII° Isothermal process



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

$$= \int_1^2 \frac{nRT}{V} \, dV$$

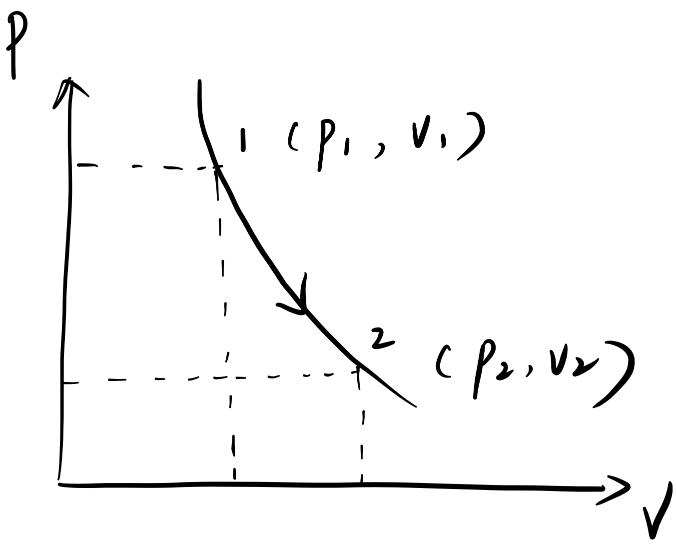
$$= nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta U = 0$$

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

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）

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

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

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

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

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

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

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

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

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

$$\gamma \int_{(p_1, V_1)}^{(p_2, V_2)} d\ln V = - \int_{(p_1, V_1)}^{(p_2, V_2)} d\ln p + c_1$$

$$\gamma \ln \frac{V_2}{V_1} = - \ln \frac{p_2}{p_1} + c_1$$

$$\left(\frac{V_2}{V_1} \right)^{\gamma} = c_2 \frac{p_1}{p_2}$$

$$p_1 V_1^{\gamma} = p_2 V_2^{\gamma} = \text{const}$$

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directly start from (*)

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

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

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

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

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

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

$$\downarrow$$

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

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

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

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

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

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

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

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

$$\downarrow \quad \begin{aligned} pV^{\gamma} &= c \\ pV &= nRT \end{aligned}$$

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

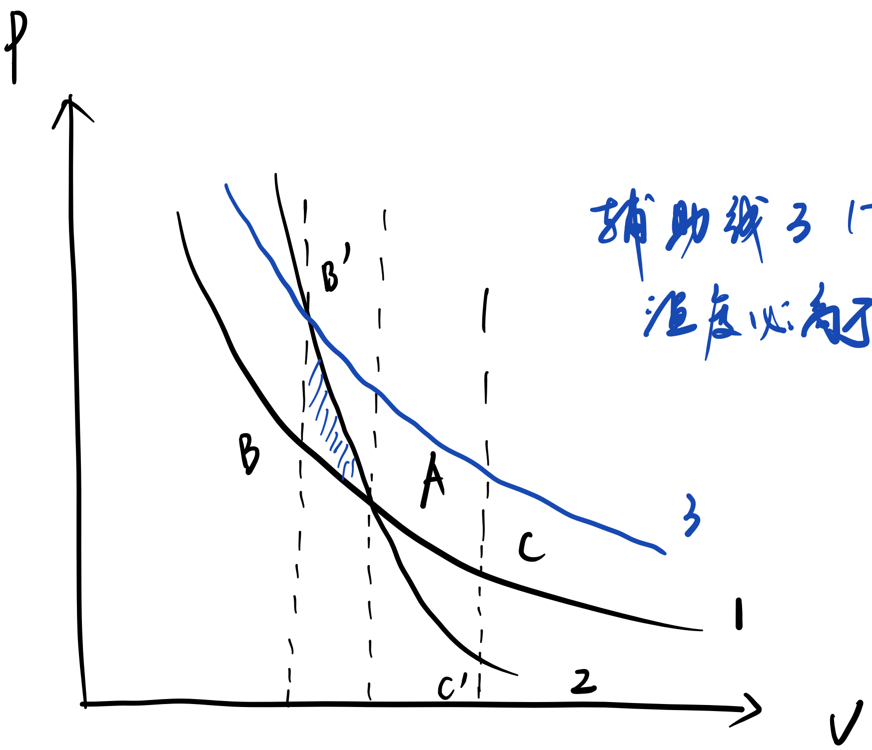
$$= \frac{c\left[\frac{nRT_2}{c} - \frac{nRT_1}{c}\right]}{1-\gamma}$$

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

$\Delta Q = \Delta U + \Delta W = 0$ （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 ?

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

$\begin{cases} B' \to A \\ B \to A \end{cases}$ $\quad T_{B'} > T_B$

$(pV = nRT)$

绝热：$\Delta U + \Delta W = 0$ 更多的作功靠降

$$\begin{cases} A \to C \\ A \to C' \end{cases}$$

内能求解

对于绝热： $dQ = dU + pdV = 0$

膨胀对外做功
以降内能，$T\downarrow$
$T_{C'} < T_C$

$$U_{C'} < U_C$$

$$pV = c_1 \quad \Rightarrow \quad p = c_1 / V \quad ①$$

$$pV^{\gamma} = c_2 \quad\quad p = c_2 / V^{\gamma} \quad ②$$

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

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

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

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

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

同为负数
绝热更陡峭

heat capacity

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

$H = U + pV$ (enthalpy : /'enθəlpi/)

$$Q = \Delta U + W$$

$$dQ = dU + p\,dV$$

(the differential form of 1st law)

$$C_V = \frac{1}{n}\left(\frac{dU}{dT}\right)_V$$

$\boxed{\text{ideal gas}}$

$$U = \frac{3}{2} N k_B T = \frac{3}{2} nRT$$

$$\left(\frac{du}{dT}\right)_V = \frac{3}{2} nR$$

$$\boxed{c_V = \frac{3}{2} R}$$

$$pV = nRT$$

$$V = \frac{nRT}{p} \qquad \frac{dV}{dT} = \frac{nR}{p}$$

$$dQ = du + p\,dV \qquad c_p \equiv \frac{1}{n}\left(\frac{dQ}{dT}\right)_p$$

$$c_p = \frac{1}{n}\left(\frac{du}{dT}\right)_p + \frac{1}{n} p \left(\frac{dV}{dT}\right)_p$$

$$= c_V + \frac{p}{n} \times \frac{nR}{p}$$

$$= c_V + R = \frac{5}{2} R$$

$$c_p = \left(\frac{dQ}{dT}\right)_p$$

$$dQ = du + p\,dV \underbrace{+ V\,dp}_{=0}$$

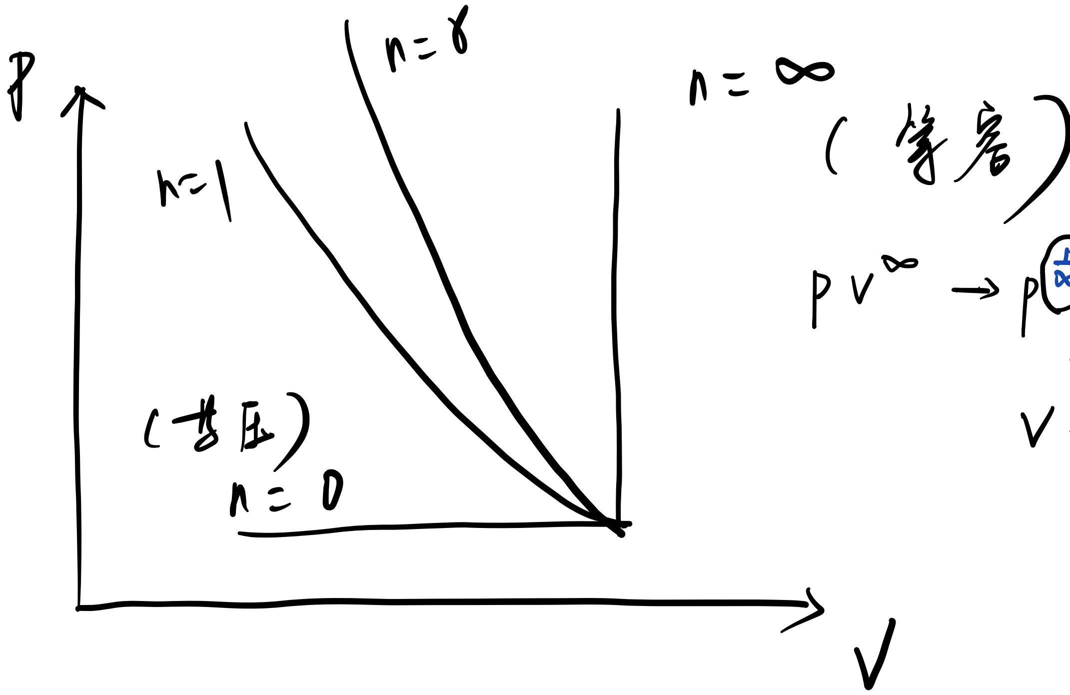
$$= du + d(pV)$$

$$c_p = c_V + R$$

c_p vs c_V : experiment vs theory

多方过程 (poly-tropic process)

$$pV^n = const$$

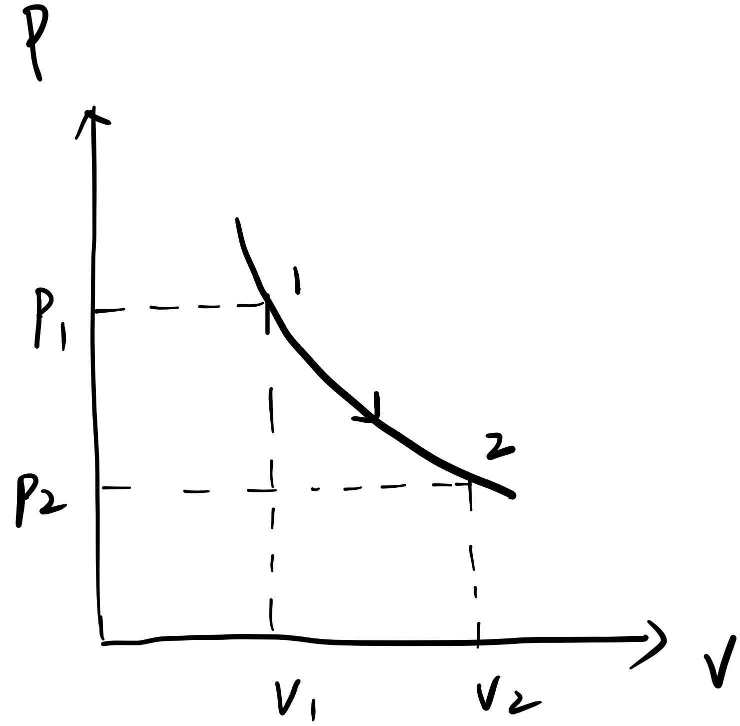


$$pV^{\infty} \rightarrow p^{\frac{1}{\infty} \rightarrow 0} V$$
$$\Downarrow$$
$$V = const$$

$$n \in (1, \gamma)$$

实际过程

$$dw = p\,dv$$



$$dQ = dU + dW$$

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

$$= \int_1^2 \frac{c}{V^n} dV = \frac{V^{1-n}}{1-n} \Big|_{V_1}^{V_2}$$

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

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

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

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

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

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

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

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

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

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

$$\Uparrow$$

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

多方 → 绝热

$$\frac{C_p}{C_V} = \frac{5}{3}$$ （单原子分子）

（C_p：体积膨胀，做功，吸更多的热）

otto cycle in thermal physics II

Lin Hsiu-Han （现在网络课程更名为热统计物理）

heat engine : A device converts "heat" into "work"