热力学第一定律： $Q = \Delta E + A \quad (dQ = dE + PdV)$

其中：$\Delta E = \dfrac{m}{M}\dfrac{i}{2}R\Delta T$ ——与过程无关的状态量

$$A = \int_{V_1}^{V_2} p\,\mathrm{d}V \text{ ——过程量}$$

$$Q = \frac{m}{M}C_{mol}\Delta T \text{ ——过程量}$$

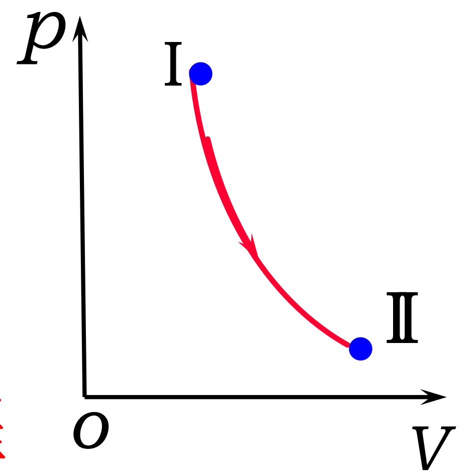
$$C_{mol} = \frac{dQ}{dT}\left\{\begin{array}{l} C_V = \dfrac{i}{2}R \\ C_P = C_V + R \end{array}\right\}\gamma = \frac{C_P}{C_V} = \frac{i+2}{i}$$

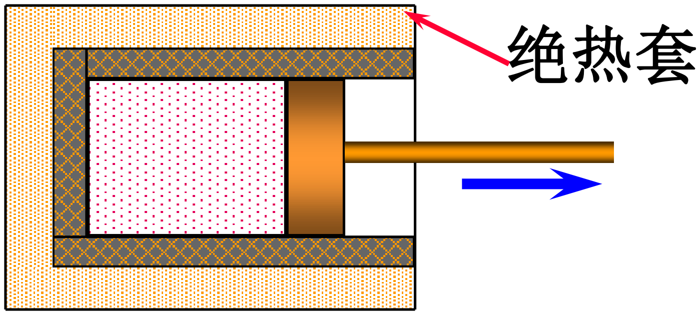
三种等值过程和绝热过程：

【p265 表7—2】

7.3 绝热过程　　多方过程

7.3.1绝热过程





特征：　$Q = 0$

一、准静态绝热过程

$$*A = -\Delta E = -\frac{m}{M}\frac{i}{2}R(T_2 - T_1) = \frac{i}{2}(P_1V_1 - P_2V_2) = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$

证明：$\frac{i}{2}(P_1V_1 - P_2V_2) = \frac{P_1V_1 - P_2V_2}{\frac{2}{i}} = \frac{P_1V_1 - P_2V_2}{\frac{2}{i}+1-1}$

$$= \frac{P_1V_1 - P_2V_2}{\frac{i+2}{i}-1} = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$

* 绝热过程中P，V，T三者同时变化

例： 绝热膨胀 V↑→A>0→△E<O→T↓→P↓

* 绝热过程的过程方程

$$\mathrm{d}A = -\,\mathrm{d}E \longrightarrow p\mathrm{d}V = -\frac{m}{M} C_V \mathrm{d}T \qquad ----(1)$$

$$pV = \frac{m}{M} RT \longrightarrow p\mathrm{d}V + V\mathrm{d}p = \frac{m}{M} R\mathrm{d}T \qquad ----(2)$$

（1）、（2）中消去dT，得：

$$(C_V + R)PdV = -C_V VdP \longrightarrow C_P \frac{dV}{V} = -C_V \frac{dP}{P}$$

$$\frac{dP}{P} = -\gamma \frac{dV}{V} \xrightarrow{\text{两边积分}} \gamma \ln V + \ln p = C \longrightarrow \ln pV^{\gamma} = C$$

$$pV^{\gamma} = C'$$

泊松方程
（绝热方程）

$$\boxed{pV^{\gamma} = C'}$$

将理想气体状态方程代入上式，并从中消去p 或V 就可以得到另外两个泊松方程：$V^{\gamma-1}T = C''$

$P^{\gamma-1}T^{-\gamma} = C'''$

* 绝热线与等温线比较

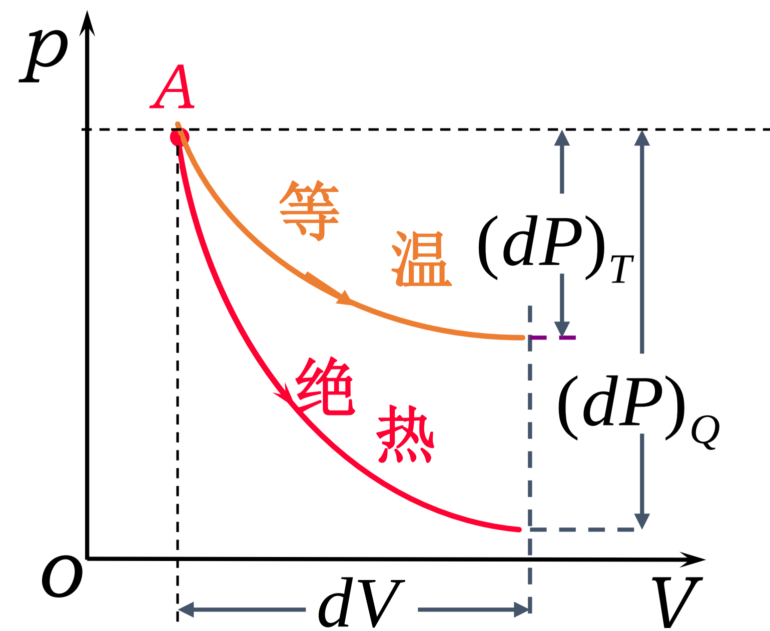
$a.$ 图形上：绝热线比等温线陡

b. 数学解释：

等温过程：$pV = C$

$\rightarrow p\,\mathrm{d}V + V\,\mathrm{d}p = 0$

$$\rightarrow \left(\frac{\mathrm{d}p}{\mathrm{d}V}\right)_T = -\frac{p}{V}$$



绝热过程： $pV^{\gamma}=C \Rightarrow \gamma pV^{\gamma-1}dV+V^{\gamma}dp=0$

$$\left(\frac{\mathrm{d}p}{\mathrm{d}V}\right)_Q=-\gamma\frac{p}{V}$$

$\because \gamma>1$

$$\therefore \left|\left(\frac{\mathrm{d}p}{\mathrm{d}V}\right)_Q\right|_A > \left|\left(\frac{\mathrm{d}p}{\mathrm{d}V}\right)_T\right|_A$$

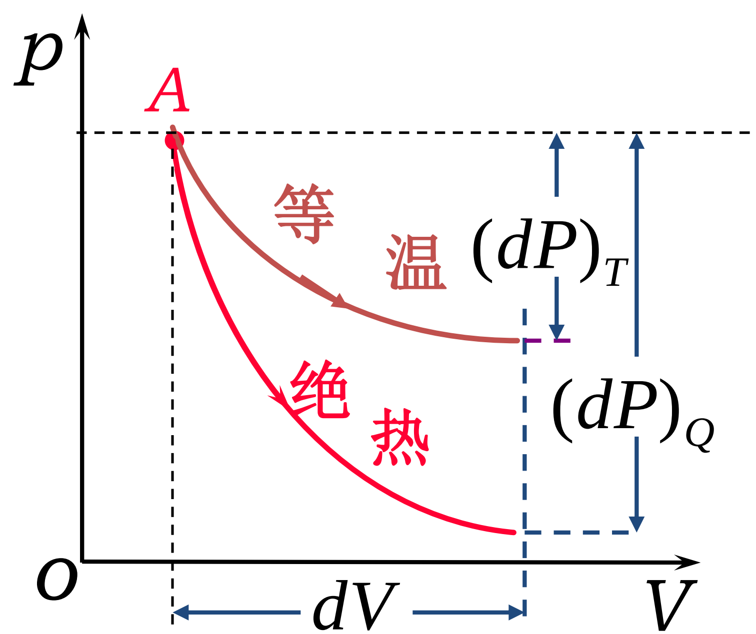
c. 物理解释：膨胀相同的体积绝热比等温压强下降得快

$\because p=\frac{2}{3}n\overline{\varepsilon_k}$

等温 $V\uparrow \rightarrow n\downarrow \rightarrow p\downarrow$

绝热 $V\uparrow \rightarrow n\downarrow \rightarrow p\downarrow$

$V\uparrow \rightarrow T\downarrow \rightarrow \overline{\varepsilon_k}\downarrow \rightarrow p\downarrow$



[例题7－1]设有8g氧气，体积为0.41×10^{-3}m^{3}, 温度为300K，如氧气作绝热膨胀，膨胀后的体积为4.10×10^{-3} m^{3}, 问气体作功多少？如氧气作等温膨胀，膨胀后的体积也是4.10×10^{-3} m^{3} ，问这时气体作功多少？

$$PV^{\gamma}=C_1$$

$$V^{\gamma-1}T=C_2$$

$$P^{\gamma-1}T^{-\gamma}=C_3$$

解： 气体若作绝热膨胀，所作的功为：

$$\left.\begin{aligned} &A=-\Delta E=\frac{m}{M_{mol}}C_V(T_1-T_2)\\ &V_1^{\gamma-1}T_1=V_2^{\gamma-1}T_2\\ &\gamma=\frac{i+2}{i}=\frac{7}{5}=1.4 \end{aligned}\right\} A=941(J)$$

气体若作等温膨胀，所作的功为：

$$A=\frac{m}{M}RT_1\ln\frac{V_2}{V_1}=1.44\times10^3(J)$$

[例题7－2] 1mol单原子理想气体，由状态a(p_1, V_1)先等压加热至体积增大1倍，再等体加热至压力增大1倍，最后再经绝热膨胀，使其温度降至初始温度，如图所示，试求：

(1) 状态d的体积V_d；

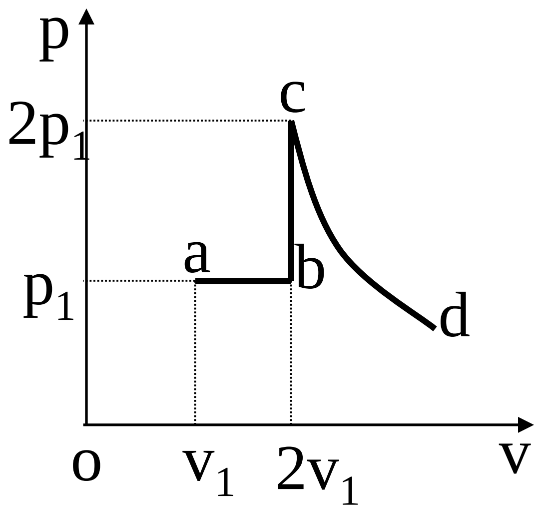
(2) 整个过程对外所做的功；

(3) 整个过程吸收的热量.

$$PV^{\gamma} = C_1$$

$$V^{\gamma-1}T = C_2$$

$$P^{\gamma-1}T^{-\gamma} = C_3$$



解：(1) 由绝热过程方程：$T_c V_c^{\gamma-1} = T_d V_d^{\gamma-1}$

$$\text{得：}\quad V_d = \left(\frac{T_c}{T_d}\right)^{\frac{1}{\gamma-1}} V_c = 15.8V_1$$

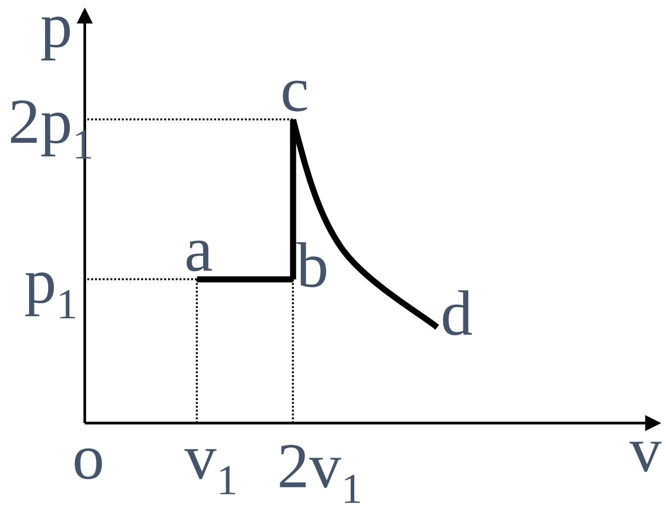
$$\text{根据题意：}\quad T_d = T_a = \frac{p_1 V_1}{R}$$

$$V_c = 2V_1$$

$$T_c = \frac{p_c V_c}{R} = \frac{4p_1 V_1}{R} = 4T_a$$

$$\gamma = \frac{5}{3}$$

(2) 整个过程对外所做的功；



$$A = A_{ab} + A_{bc} + A_{cd} = \frac{11}{2}P_1V_1$$

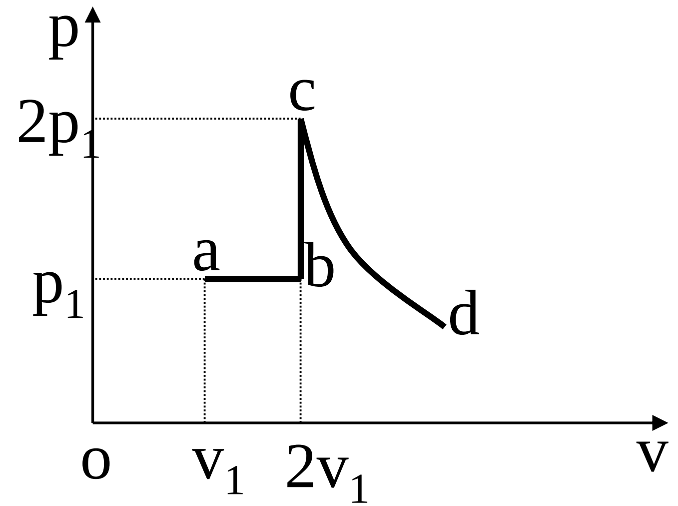
其中：$A_{ab} = p_1(V_b - V_a) = p_1V_1$

$$A_{bc} = 0$$

$$A_{cd} = -\Delta E_{cd} = C_V(T_c - T_d) = C_V(4T_a - T_a)$$

$$= \frac{3}{2}R \cdot 3T_a = \frac{9}{2}p_1V_1$$

(3) 整个过程吸收的热量.



方法一：$Q = Q_{ab} + Q_{bc} + Q_{cd} = \dfrac{11}{2} P_1 V_1$

$$Q_{ab} = C_p (T_b - T_a) = \frac{5}{2} R(T_b - T_a)$$

$$= \frac{5}{2}(p_b V_b - p_a V_a) = \frac{5}{2} p_1 V_1$$

$$Q_{bc} = C_V (T_c - T_b) = \frac{3}{2} R(T_c - T_b) = \frac{3}{2}(p_c V_c - p_b V_b) = 3 p_1 V_1$$

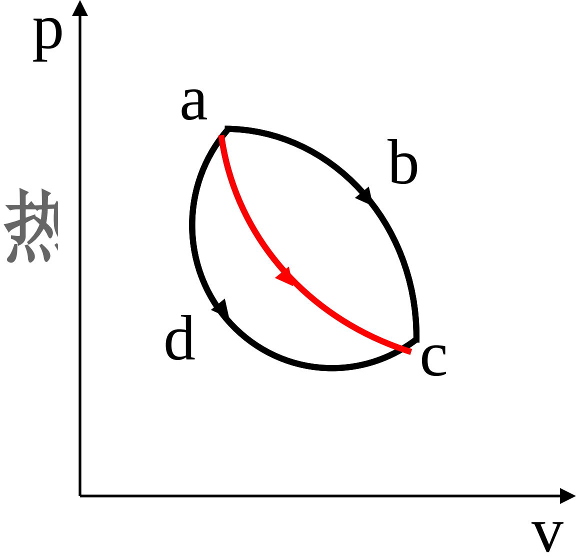
$$Q_{cd} = 0$$

方法二：对abcd整个应用热力学第一定律 $Q = \Delta E + A$

$$\because \quad T_a = T_d \,, \Delta E = 0 \qquad \therefore Q = A = \frac{11}{2} p_1 V_1$$

[例题7—3]　若$a \to c$过程是绝热过程

问：abc过程和adc过程是吸热还是放热



$\because$ 三过程始末状态均相同

$\therefore \Delta E_{abc} = \Delta E_{ac} = \Delta E_{adc} = \Delta E$

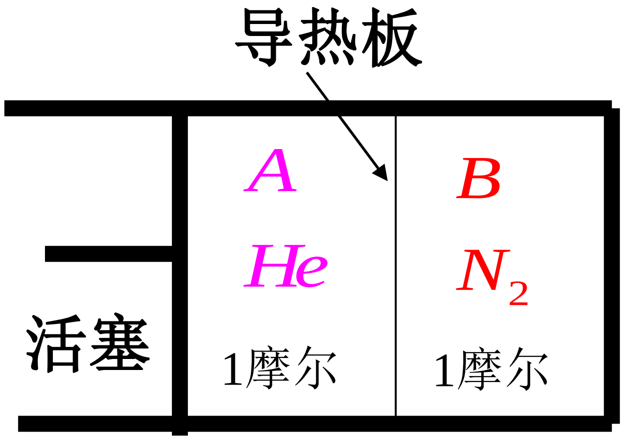
$$\left.\begin{array}{l} \text{又}\because a \to c \quad (Q = 0) \\ A_{ac} = -\Delta E \\ \text{而} A_{ac} > 0 \end{array}\right\} \therefore \Delta E < 0$$

$$abc\text{过程：}\left.\begin{array}{l} Q_{abc} = A_{abc} + \Delta E \\ A_{abc} > A_{ac} \end{array}\right\} Q = (A_{abc} - A_{ac}) > 0 \ \text{（吸热）}$$

$$adc\text{过程：}\left.\begin{array}{l} Q_{adc} = A_{adc} + \Delta E \\ A_{adc} < A_{ac} \end{array}\right\} Q_{adc} = (A_{adc} - A_{ac}) < 0 \ \text{(放热)}$$

[例题7—4] 汽缸、活塞均绝热，活塞在外力作用下缓慢移动，对He作功A'。求：N_2内能的变化。

解：$\Delta E_{N_2} = \frac{5}{2}R\Delta T_B = \frac{5}{8}A'$



$\{A, B\} \because Q = 0$

$$\therefore A' = \Delta E = \Delta E_A + \Delta E_B$$

$$= \frac{3}{2}R\Delta T_A + \frac{5}{2}R\Delta T_B = \frac{8}{2}R\Delta T \Rightarrow \Delta T = \frac{A'}{4R}$$

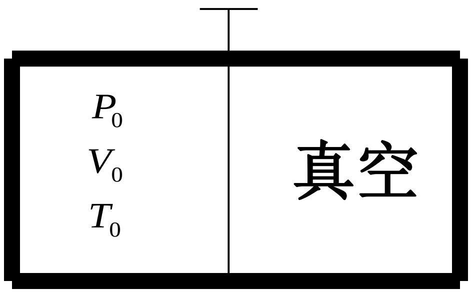
又$\because$准静态过程$\therefore \Delta T_A = \Delta T_B$

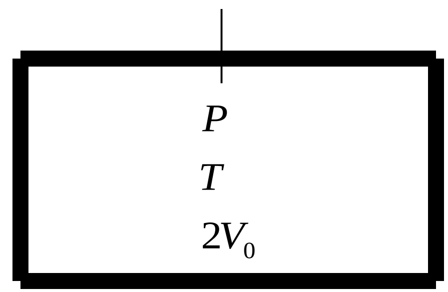
二、非静态绝热过程——绝热自由膨胀

$PV^{\gamma} = C_1$

$V^{\gamma-1}T = C_2$

$P^{\gamma-1}T^{-\gamma} = C_3$





$V_0^{\gamma-1}T_0 = (2V_0)^{\gamma-1}T \rightarrow T$

$P_0V_0^{\gamma} = P\,(2V_0)^{\gamma} \rightarrow P$

∵绝热过程

$$\left.\begin{array}{l} \therefore (E - E_0) + A = 0 \\ \text{而} \quad A = 0 \end{array}\right\} \quad E = E_0 \qquad (T = T_0)$$

始末两态满足状态方程 $\dfrac{P_0V_0}{T_0} = \dfrac{P\,(2V_0)}{T} \Longrightarrow P = \dfrac{1}{2}P_0$

三、多方过程

*过程方程

$$pV^n = C \qquad n \longrightarrow \text{多方指数}$$

n =1 —— 等温过程　　n =γ —— 绝热过程

n= 0 —— 等压过程　　n =∞ —— 等容过程

$$PV^n = C \Rightarrow P^{\frac{1}{n}}V = C' \xrightarrow[P^{\frac{1}{n}}=1]{n=\infty} V = C'$$

*多方过程的功

$$\left.\begin{aligned} A &= \int_{V_1}^{V_2} PdV \\ PV^n &= P_1V_1^n \end{aligned}\right\} A = P_1V_1^n \int_{V_1}^{V_2} \frac{dV}{V^n} = P_1V_1^n\left[\frac{1}{1-n}V_2^{1-n} - \frac{1}{1-n}V_1^{1-n}\right]$$

利用：$P_1V_1^{\ n} = P_2V_2^{\ n}$

$$= \frac{P_1V_1 - P_2V_2}{n-1}$$

*摩尔热容

$$A=\frac{P_1V_1-P_2V_2}{n-1}=-\frac{1}{n-1}\left[\frac{m}{M}R(T_2-T_1)\right]$$

$$\Delta E=\frac{m}{M}C_V(T_2-T_1)$$

$$Q=A+\Delta E=\frac{m}{M}\left[C_V-\frac{R}{n-1}\right](T_2-T_1)=\frac{m}{M}C_{mol}\Delta T$$

$$C_{mol}=C_V-\frac{R}{n-1}=\frac{nC_V-C_V-R}{n-1}=\frac{nC_V-C_P}{n-1}$$

$$=\frac{nC_V-\gamma C_V}{n-1}=\frac{n-\gamma}{n-1}C_V$$

等压过程：$n=0, C_{mol}=\gamma C_V=C_P$ 等容过程：$n=\infty, C_{mol}=C_V$

等温过程：$n=1, C_{mol}=\infty$ 绝热过程：$n=\gamma, C_{mol}=0$

$$又\because C_{mol}=\frac{dQ}{dT}=\frac{n-\gamma}{n-1}C_V$$

$$\therefore 当\quad n>\gamma 或 n<1 时\quad C_{mol}>0\begin{cases}T\uparrow & Q>0 & 吸热\\ T\downarrow & Q<0 & 放热\end{cases}$$

$$\therefore 当\quad 1<n<\gamma 时,\quad C_{mol}<0\begin{cases}T\uparrow & Q<0 & 放热\\ T\downarrow & Q>0 & 吸热\end{cases}$$