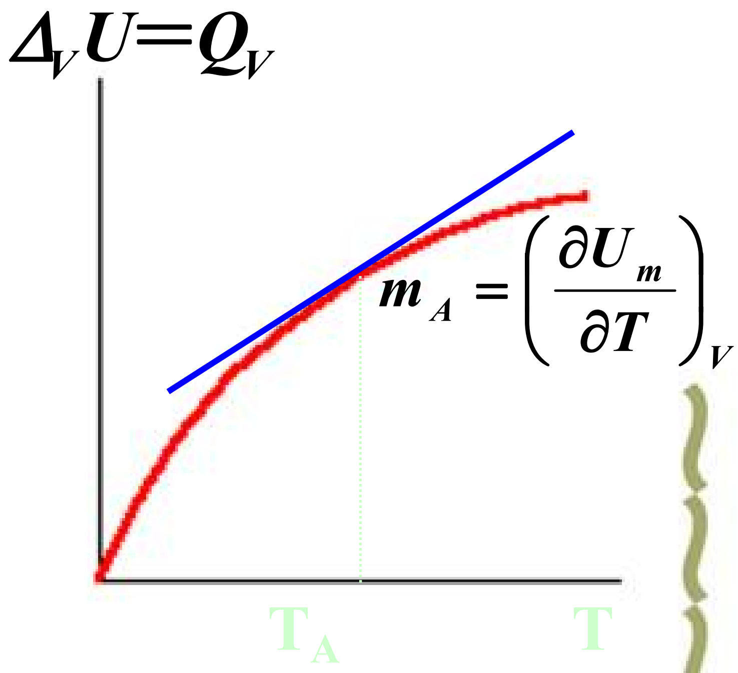
C_m 随温度的变化

$$C_{p,m} = a + bT + cT^2 + dT^3$$

$$C_{p,m} = a' + b'T + c'T^{-2}$$



平均摩尔定压热容

$$\overline{C}_{p,m} = \frac{Q_{p,m}}{T_2 - T_1} = \frac{\int_{T_1}^{T_2} C_{p,m} dT}{T_2 - T_1}$$

$$\overline{C}_{p,m} = \frac{1}{2}\left[C_{p,m}(T_1) + C_{p,m}(T_2)\right]$$

$$\overline{C}_{p,m} = C_{p,m}\left(\overline{T}\right) \qquad \overline{T} = \frac{1}{2}\left(T_1 + T_2\right)$$

$C_{V,m}$和$C_{p,m}$ 的关系

$$C_{p,m} - C_{V,m} = \left(\frac{\partial H_m}{\partial T}\right)_p - \left(\frac{\partial U_m}{\partial T}\right)_V = \left\{\frac{\partial\left(U_m + pV_m\right)}{\partial T}\right\}_p - \left(\frac{\partial U_m}{\partial T}\right)_V$$

$$= \left(\frac{\partial U_m}{\partial T}\right)_p + p\left(\frac{\partial V_m}{\partial T}\right)_p - \left(\frac{\partial U_m}{\partial T}\right)_V$$

由$U_m = f$（T，V）得：

$$dU_m = \left(\frac{\partial U_m}{\partial T}\right)_V dT + \left(\frac{\partial U_m}{\partial V_m}\right)_T dV_m$$

恒压下，可得：

$$\left(\frac{\partial U_m}{\partial T}\right)_p = \left(\frac{\partial U_m}{\partial T}\right)_V + \left(\frac{\partial U_m}{\partial V_m}\right)_T \left(\frac{\partial V_m}{\partial T}\right)_p$$

将上式代入（$C_{p,m}$- $C_{V,m}$）的式子中：

$$C_{p,m}-C_{V,m}=\left[\left(\frac{\partial U_m}{\partial V_m}\right)_T+p\right]\left(\frac{\partial V_m}{\partial T}\right)_p$$

恒压过程，温度升高体积膨胀，导致：

1.系统内部分子势能升高，热力学能增加；

2. 对环境做功。

因此$C_{p,m}$总是大于$C_{V,m}$

对理想气体

$$p\left(\frac{\partial V_m}{\partial T}\right)_p=p\left(\frac{\partial\left(\frac{RT}{p}\right)}{\partial T}\right)_p=p\frac{R}{p}=R$$

$C_{p,m}-C_{V,m}=R$

对液体与固体

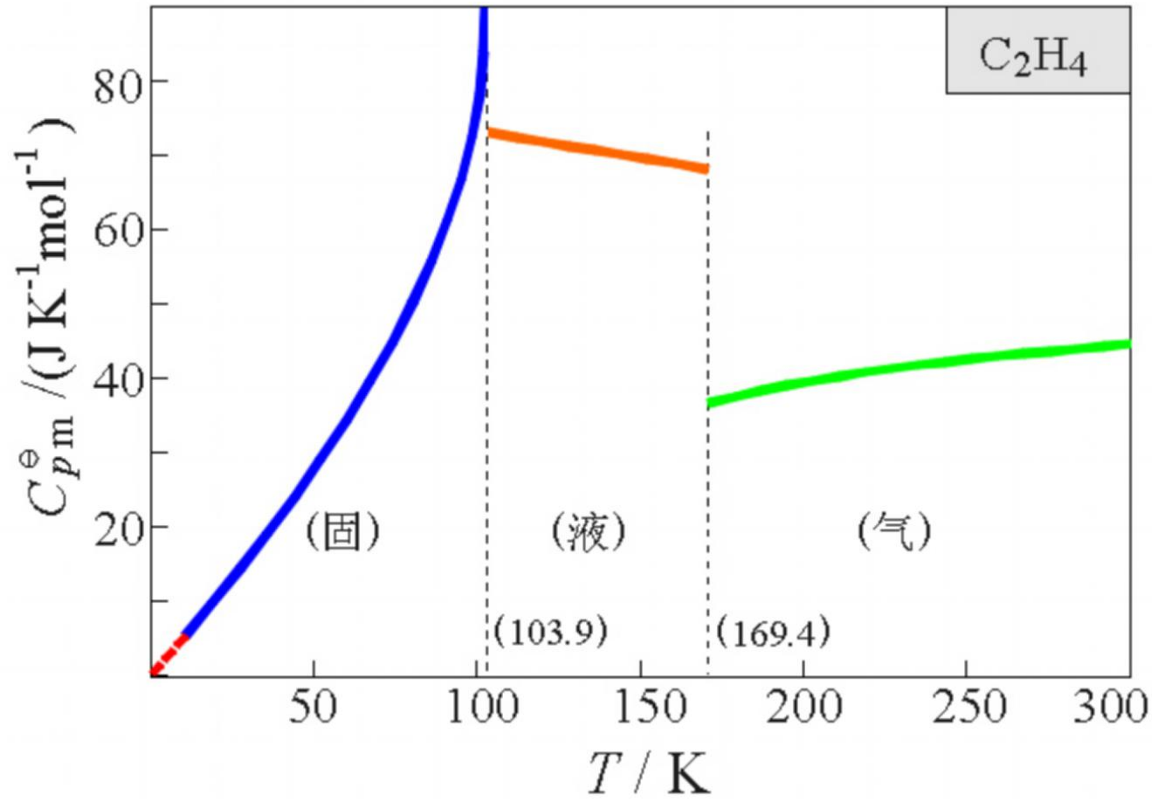
$$\left(\frac{\partial V_m}{\partial T}\right)_p\approx 0$$

$C_{p,m}-C_{V,m}\approx 0$

◆热容是物质的特性

◆同一物质，聚集状态不同，热容不同

◆热容是温度的函数



◆理想气体的摩尔热容

单原子气体 $C_{V,m} = 3R/2$ $\quad C_{p,m} = 5R/2$

双原子气体 $C_{V,m} = 5R/2$ $\quad C_{p,m} = 7R/2$

2. 恒容变温及恒压变温过程热的计算

对于n一定的某系统进行单纯pVT变化

$$C_{V,\mathrm{m}} \overset{\mathrm{def}}{=\!=} \frac{\delta Q_V}{dT} = \left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_V \longrightarrow Q_V = \Delta U_V = n\int_{T_1}^{T_2} C_{V,m}\,dT$$

$$C_{p,\mathrm{m}} \overset{\mathrm{def}}{=\!=} \frac{\delta Q_p}{dT} = \left(\frac{\partial H_\mathrm{m}}{\partial T}\right)_p \longrightarrow Q_p = \Delta H_p = n\int_{T_1}^{T_2} C_{p,m}\,dT$$

若$C_{V,m}$为常数，则 $Q_V = \Delta U_V = nC_{V,m}\Delta T$

若$C_{p,m}$为常数，则 $Q_p = \Delta H_p = nC_{p,m}\Delta T$

3. 凝聚系统变温过程

因为C

$$Q_V = Q_p = \Delta H_p = n\int_{T_1}^{T_2} C_{p,m}\,dT$$

§ 2.5　焦耳实验、理想气体的U与H

1. 焦耳实验

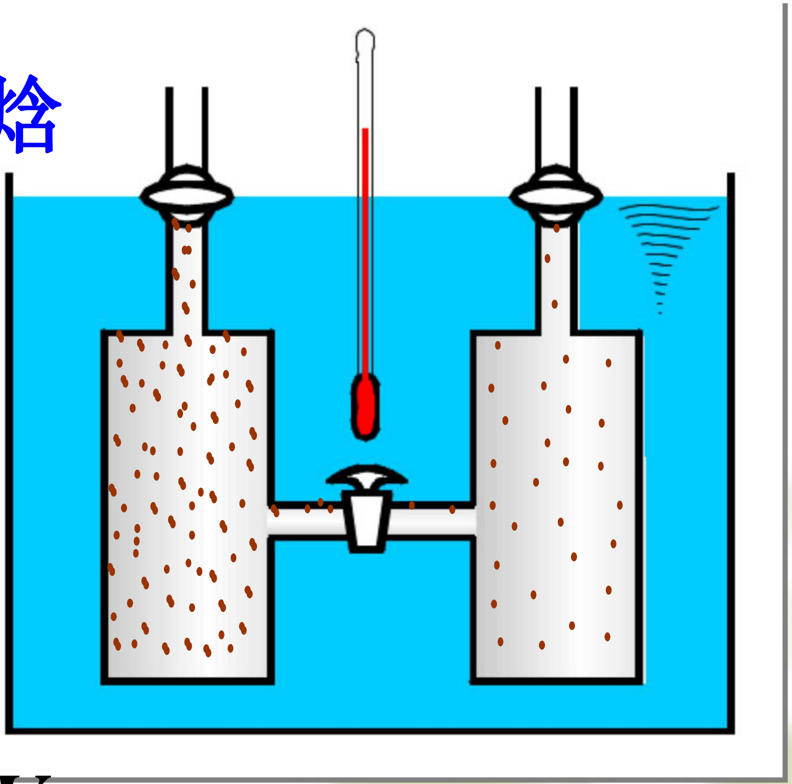
2. 理想气体的热力学能与焓

$W = 0$　　$Q = 0$

$\Delta U = 0$

$\mathrm{d}T = 0$　　$\mathrm{d}U = 0$

$\mathrm{d}V > 0$　　$\mathrm{d}p < 0$



$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

理想气体$U=f(T)$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \text{ 同理} \left(\frac{\partial U}{\partial p}\right)_T = 0$$

对于无相变及化学变化的

理想气体等温过程：$\Delta U=0$

$$H=U+pV$$

$$\left(\frac{\partial H}{\partial p}\right)_T=\left(\frac{\partial U}{\partial p}\right)_T+\left(\frac{\partial (pV)}{\partial p}\right)_T=0+\left(\frac{\partial (nRT)}{\partial p}\right)_T=0$$

同理 $\left(\frac{\partial H}{\partial V}\right)_T=0$

对于无相变及化学变化的理想气体等温过程：

$$\Delta H=0$$

对于理想气体 $U = f(T,V), H = f(T,P)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = \left(\frac{\partial U}{\partial T}\right)_V dT + 0$$

$$= n\left(\frac{\partial U_m}{\partial T}\right)_V dT = nC_{V,m}dT$$

$$\Delta U = n\int_{T_1}^{T_2} C_{V,m}dT$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp = \left(\frac{\partial H}{\partial T}\right)_p dT + 0$$

$$= n\left(\frac{\partial H_m}{\partial T}\right)_p dT = nC_{p,m}dT$$

$$\Delta H = n\int_{T_1}^{T_2} C_{p,m}dT$$

说明对于理想气体，ΔU与ΔH的计算不再受过程恒容与恒压条件的限制。

❖ 例：将10.0g 523K、2.00×10⁵Pa的CO(g)等压降温到273K，计算此过程的Q、ΔU、ΔH。已知在此温度区间 $\overline{C}_{p,m}(CO,g)=29.50J\cdot K^{-1}\cdot mol^{-1}$。

$$\text{解：}\quad n=\frac{m}{M}=\frac{10.0}{28.01}mol=0.375mol$$

$$Q_p=\Delta H=n\overline{C}_{p,m}(T_2-T_1)=-2.63kJ$$

$$(1)\Delta U=\Delta H-\Delta(pV)=\Delta H-\Delta(nRT)$$

$$=\Delta H-nR\Delta T=-1.89kJ$$

$$(2)\overline{C}_{V,m}=\overline{C}_{p,m}-R=21.19kJ\cdot K^{-1}\cdot mol^{-1}$$

$$\Delta U=n\overline{C}_{V,m}(T_2-T_1)=-1.89kJ$$

等压过程

$\Delta U_p = U_2 - U_1$

末态（1）
$T_2 = 273K$
$P_1 = 2.00 \times 10^5 Pa$
$V_2 = 4.05 \times 10^{-3} m^3$
U_2、H_2

$\Delta U_T = 0$

初态
$T_1 = 523K$
$P_1 = 2.00 \times 10^5 Pa$
$V_1 = 7.76 \times 10^{-3} m^3$
U_1、H_1

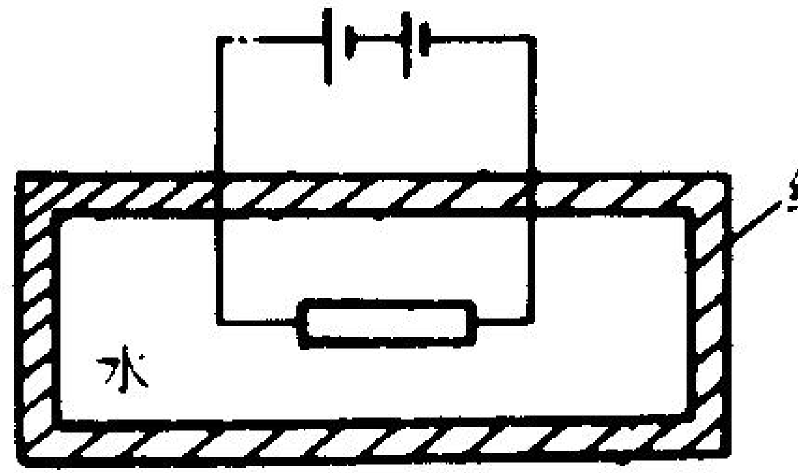
等容过程

$\Delta U_V = U_2' - U_1$

末态（2）
$T_2 = 273K$
$P_2 = 1.04 \times 10^5 Pa$
$V_1 = 7.76 \times 10^{-3} m^3$
U_2'、H_2'

$$\Delta U_p = \Delta U_V = n\overline{C}_{V,m}(T_2 - T_1)$$

例1：将一电炉丝浸入刚性绝热容器的水中，接上电源通电一段时间，试判断此过程中(a)水的热力学能，(b)水和电炉丝总的热力学能是增加、减少还是不变？



解： (a)$Q>0, W=0$, $\Delta U=Q+W>0$

(b)$Q=0, W>0$, $\Delta U=Q+W>0$

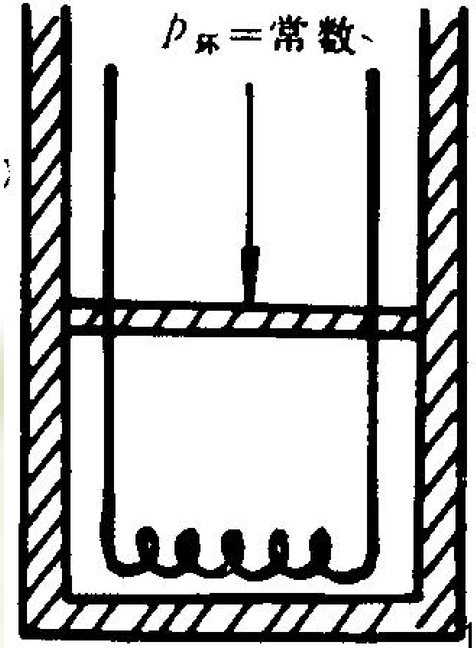
例2： 在一个带有无摩擦、无重量的绝热活塞的绝热气缸内充入一定量的气体。气缸内壁绕有电阻丝，活塞上方施以一恒定压力，并与缸内气体成平衡状态，如右图所示。现通入一微小电流，使气体缓慢膨胀。此过程为一等压过程，故 $Q_p = \Delta H$，而该系统为一绝热系统，则 $Q_p = 0$，所以此过程的 $\Delta H = 0$。此结论

(1) 以气体为系统：

$\because W' = 0, Q > 0, \therefore Q_p = \Delta H > 0$

(2) 以气体＋电阻丝为系统：

$\because W' > 0, Q = 0, \therefore Q_p \neq \Delta H$



例3： 在炎热的夏天，有人提议打开室内正在运行的冰箱的门，以降低室温，你认为此建议可行吗？

$$Q = 0, W > 0 \Rightarrow \Delta U = Q + W > 0$$

$$\Delta U = C_{V,m}(T_2 - T_1) > 0 \Rightarrow T_2 > T_1$$

上次课主要内容

1. 恒容热、恒压热、焓

$H=U+pV$　　$Q_V=\Delta U$　　$Q_p=\Delta H$

2. 恒容变温及恒压变温过程热的计算

$$C_{V,\mathrm{m}} \overset{\mathrm{def}}{=\!=} \frac{\delta Q_V}{dT} = \left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_V \longrightarrow Q_V = \Delta U_V = n\int_{T_1}^{T_2} C_{V,m}\,dT$$

$$C_{p,\mathrm{m}} \overset{\mathrm{def}}{=\!=} \frac{\delta Q_p}{dT} = \left(\frac{\partial H_\mathrm{m}}{\partial T}\right)_p \longrightarrow Q_p = \Delta H_p = n\int_{T_1}^{T_2} C_{p,m}\,dT$$

对理想气体 $C_{p,m}-C_{V,m}=R$

对液体与固体 $C_{p,m}-C_{V,m}\approx 0$

3. 理想气体的热力学能与焓

$$\left(\frac{\partial U}{\partial V}\right)_T=0 \qquad \left(\frac{\partial U}{\partial p}\right)_T=0$$

$$\left(\frac{\partial H}{\partial V}\right)_T=0 \qquad \left(\frac{\partial H}{\partial p}\right)_T=0$$

$$\Delta U=n\int_{T_1}^{T_2}C_{V,m}dT \qquad \Delta H=n\int_{T_1}^{T_2}C_{p,m}dT$$

§2·6 可逆过程与绝热过程

1. 可逆体积功

$$W_a = -p_{环}\Delta V = -18.0kJ$$

$$W_b = -\Sigma p_{环}\Delta V = [-2\times(12-6)$$

$$-1\times(24-12)]kJ = -24.0kJ$$

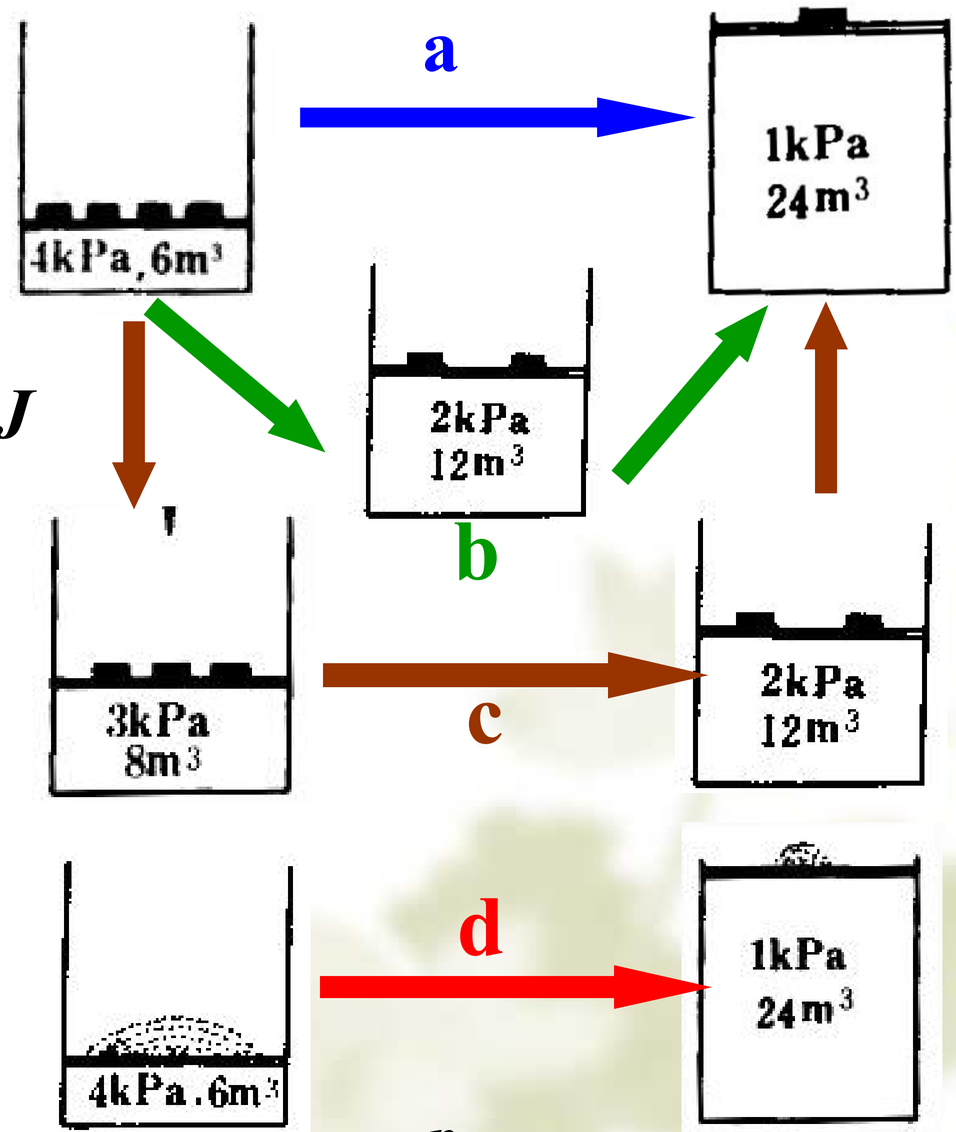
$$W_c = -26.0kJ$$

$$W_d = -\int_{V_1}^{V_2} p_{环} dV$$

$$= -\int_{V_1}^{V_2}(p-dp)dV$$

$$= -\int_{V_1}^{V_2} pdV = \int_{V_1}^{V_2}\frac{nRT}{V}dV$$

$$= nRT\ln\frac{V_1}{V_2} = nRT\ln\frac{p_2}{p_1}$$



$$W_d = p_1V_1\ln\frac{p_2}{p_1} = -33.3kJ$$

将以上过程逆向进行

$W_{a'} = 72.0kJ$

$W_{b'} = 48.0kJ$

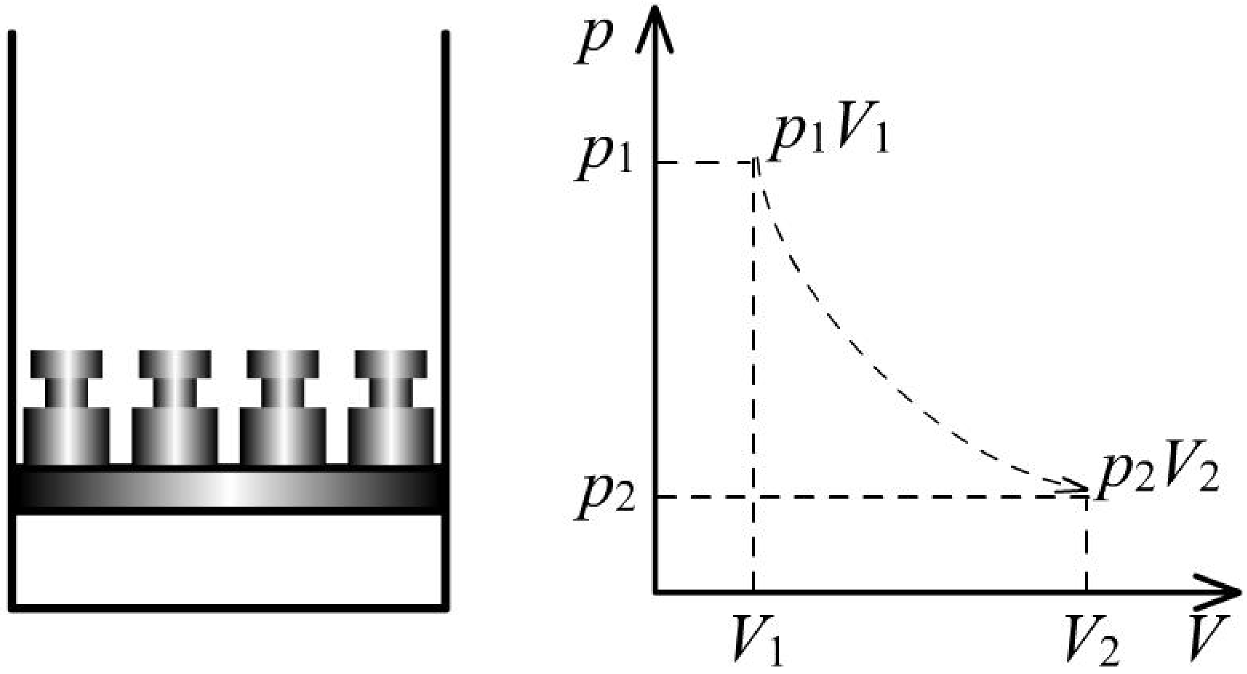
$W_{c'} = 44.0kJ$

$W_{d'} = 33.3kJ$

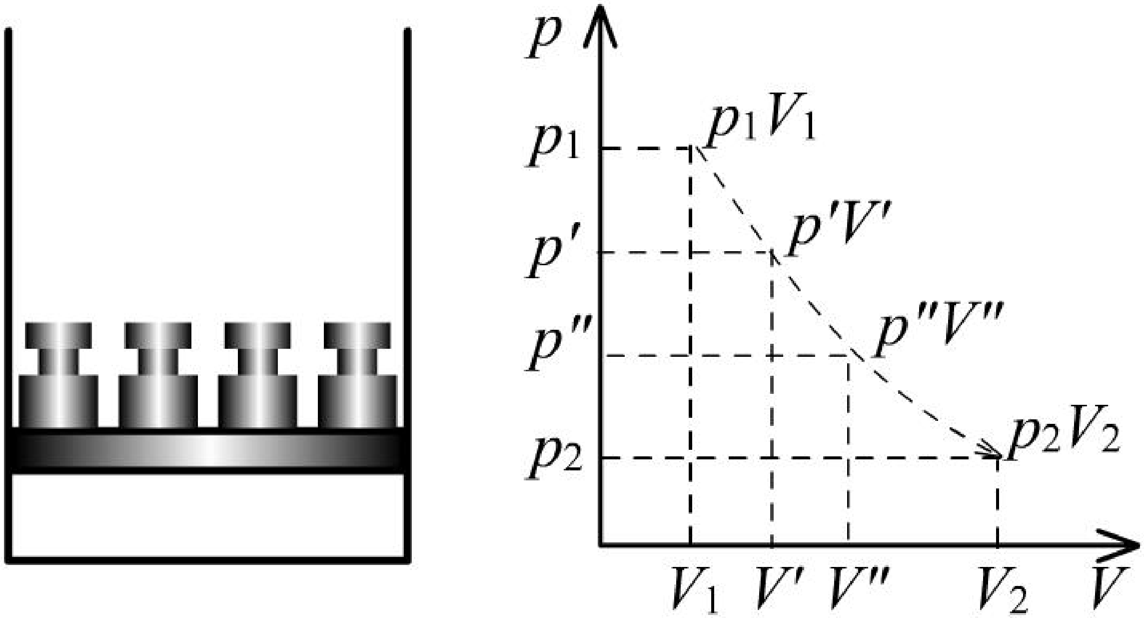
膨胀(压缩)方式	一次	二次	三次	多次
W(膨胀)/kJ	-18	-24	-26	-33.3
W(压缩)/kJ	72	48	44	33.3
∑W/kJ	54	24	18	0
∑Q/kJ	-54	-24	-18	0

在同样的初末态之间进行的等温过程中，可逆膨胀时，系统对环境作最大功；可逆压缩时，环境对系统作最小功。

一次等外压膨胀



多次等外压膨胀



可逆膨胀