2024秋物理化学I第一次测验

1. $R = \underbrace{k_B}_{J\cdot K^{-1}} \overbrace{N_A}^{mol^{-1}} \Rightarrow A$

2. velocity distribution $\Rightarrow$ each DoF gives $k_BT/2$ $\Rightarrow$ C.

3. 相互碰撞 × 碰撞器壁 ✓ $\Rightarrow A$

   p 守恒　　p 改变

4. $r \propto M^{-1/2}$

   $r = \frac{1}{4} n\langle v\rangle = \frac{p}{\sqrt{2\pi m k_B T}}$　　$\frac{r_{235UF_6}}{r_{238UF_6}} = \sqrt{\frac{M_{238UF_6}}{M_{235UF_6}}} = D.$

5. $p_{gas} = p_{exterior} \Rightarrow C.$

6. Consider $\left(\frac{\partial U}{\partial V}\right)_T$ and $\left(\frac{\partial H}{\partial p}\right)_T$:

$$\left.\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial p}{\partial T}\right)_V - p = T\cdot\frac{R}{V_m - b} - p = 0 \\ \left(\frac{\partial H}{\partial p}\right)_T &= V - T\left(\frac{\partial V}{\partial T}\right)_p = V - T\cdot\frac{nR}{p} = nb > 0 \end{aligned}\right\} \Rightarrow C.$$

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

   so $\left(\frac{\partial U}{\partial V}\right)_T = 0$ is demanded $\Rightarrow$ B.

8. 排斥势为刚球势 $\Rightarrow$ B.

9. 准静态过程中，热量具有态函数表示：

$$đQ = \left(\frac{\partial Q}{\partial T}\right)_V dT + A\,dV = C_V dT + A\,dV$$

$$đQ = \left(\frac{\partial Q}{\partial T}\right)_p dT + B\,dp = C_p dT + B\,dp$$

其中 A, B 皆为系统的态函数，则

$$(C_p - C_V)dT + B\,dp - A\,dV = 0$$

给出 T, p, V 间偏导数：

$$\left(\frac{\partial p}{\partial V}\right)_T = A/B,$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{C_p - C_V}{A},$$

现考虑绝热过程 $đQ = 0 \Rightarrow$

$$C_V dT + A\,dV = 0 \Rightarrow C_p dT + \frac{C_p}{C_V} A\,dV = 0 \Rightarrow$$

$$\gamma A\,dV = B\,dp \Rightarrow \left(\frac{\partial p}{\partial V}\right)_{đQ} = \gamma A/B = \gamma \left(\frac{\partial p}{\partial V}\right)_T,$$

$$\left(\frac{\partial V}{\partial T}\right)_{đQ} = -\frac{C_V}{A} = -\frac{C_V}{C_p - C_V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{1-\gamma}\left(\frac{\partial V}{\partial T}\right)_p. \Rightarrow B.$$

10.

$$\langle v \rangle = \sqrt{\frac{8RT}{\pi M}} = 474.65 \qquad \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3RT}{M}} = 515.18.$$

$$\Gamma = \frac{1}{4} n \langle v \rangle = \frac{p}{\sqrt{2\pi m k_B T}} = 3.155e+27$$

$$Z = n\sigma\langle v \rangle\sqrt{2} = 8.063e+8.$$

$$\lambda = \frac{1}{\sqrt{2} n\sigma} = 5.887e-7 \Rightarrow B.$$

11.

(1)

$$\left(p+\frac{a}{V_m^2}\right)(V_m-b)=RT$$

$$\text{or} \quad p=\frac{RT}{V_m-b}-\frac{a}{V_m^2} \qquad 3'$$

23.

(2)

随 $\rho\to 0$, i.e. $V_m\to\infty$. 气体回归理想气体 2'

$$\lim_{\rho\to 0} Z = 1 \Rightarrow A = 1. \qquad 2'$$

(3)

$$\left(\frac{\partial Z}{\partial p}\right)_T=\left(\frac{\partial Z}{\partial \rho}\right)_T\left(\frac{\partial \rho}{\partial p}\right)_T \quad 1', \quad p\to 0 \Rightarrow V_m\to\infty \Rightarrow \rho\to 0$$

$$\lim_{p\to 0^+}\left(\frac{\partial \rho}{\partial p}\right)_T=\lim_{p\to 0}\left(\frac{\partial(1/V_m)}{\partial(RT/V_m)}\right)_T=\frac{1}{RT} \quad \underline{\text{极限存在}}.\ \text{故} \qquad 2'$$

$$\lim_{p\to 0^+}\left(\frac{\partial Z}{\partial p}\right)_T=\lim_{p\to 0^+}\left(\frac{\partial Z}{\partial \rho}\right)_T\cdot\frac{1}{RT}=0 \Rightarrow$$

$$\lim_{p\to 0^+}\left(\frac{\partial Z}{\partial \rho}\right)_T=0 \quad 2' \quad \Rightarrow \quad B[T_B]=0. \qquad 2'$$

(4)

$$Z=\frac{pV_m}{RT}=\frac{V_m}{V_m-b}-\frac{a}{RT}\frac{1}{V_m} \qquad 3'$$

$$=\frac{1}{1-b\rho}-\frac{a}{RT}\rho,$$

taylor series: $\frac{1}{1-x}=1+x+x^2+x^3+o(x^3)$ for $|x|<1$,

$$Z=1+\left(b-\frac{a}{RT}\right)\rho+b^2\rho^2+b^3\rho^3+o(\rho^3) \qquad 5'$$

$$T_B=\frac{a}{bR}. \qquad 1'$$

20

12.

$$pV^{\delta} = Const, \quad pV = nRT,$$

$$p_2 V_2^{\delta} = p_1 V_1^{\delta} \Rightarrow p_2 = p_1 2^{-\delta}, \Rightarrow T_2 = \frac{T_0}{2^{\delta-1}} \qquad 2'$$

$$dU = C_V dT = \frac{3n}{2} R dT \Rightarrow$$

$$\Delta U = \frac{3n}{2} R \Delta T = \frac{3n}{2} R \left(\frac{T_0}{2^{\delta-1}} - T_0 \right) = 3nRT_0 \left(\frac{1}{2^{\delta}} - \frac{1}{2} \right). \qquad 3'$$

$$d(pV^{\delta}) = 0, \quad d(pV) = nRdT,$$

$$Vdp = -\delta p dV \Rightarrow -\delta p dV + p dV = nRdT \Rightarrow$$

$$pdV = \frac{nR}{1-\delta} dT, \qquad 3'$$

$$W = -\int p dV = \frac{nR}{\delta - 1} \Delta T = \frac{2nRT_0}{\delta-1} \left(\frac{1}{2^{\delta}} - \frac{1}{2} \right) \qquad 3'$$

$$Q = \Delta U - W = \left(3 - \frac{2}{\delta - 1} \right) nRT_0 \left(\frac{1}{2^{\delta}} - \frac{1}{2} \right). \qquad 1'$$

对于$\delta=1$的等温过程

$$\Delta U = 0, \qquad 1'$$

$$W = \lim_{\delta \to 1} \frac{2nRT_0}{\delta - 1} \frac{1 - 2^{\delta-1}}{2^{\delta}} = nRT_0 \lim_{\delta \to 1} \frac{1 - 2^{\delta - 1}}{\delta - 1} = -nRT_0 \ln 2. \qquad 3'$$

等温算法: $W = -\int p dV = -\int \frac{nRT_0}{V} dV = -nRT_0 \ln 2 \qquad 3'$

$Q = \Delta U - W$ 自然正确. $\qquad 1'$

13. 47.

Diesel 循环，仅只有两步Q，为高温放热 Q_h，低温吸热 Q_l.

$1 \to 2 \to 3 \to 4 \to 1$

$Q_{23} = C_p(T_3 - T_2) > 0$, $\quad Q_{41} = C_V(T_1 - T_4) < 0$.

气体 $W<0$，$Q>0$ 故 Q_{23} 为 Q_h，Q_{41} 为 Q_l. 2'

so that $$\eta = \frac{C_p(T_3 - T_2) + C_V(T_1 - T_4)}{C_p(T_3 - T_2)}$$

$$= 1 - \frac{C_V}{C_p}\frac{T_4 - T_1}{T_3 - T_2}$$

$$= 1 - \frac{1}{\gamma}\frac{T_1}{T_2}\frac{T_4/T_1 - 1}{T_3/T_2 - 1}$$

$pV = Nk_B T$,

$pV^\gamma = \text{Const} \Rightarrow$

$TV^{\gamma-1} = \text{Const}$

5'

$$\cancel{\frac{T_4}{T_1} =} \quad \frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \beta^{1-\gamma}$$

$$\frac{T_3}{T_2} = \frac{V_3}{V_2} = \alpha,$$

$$\frac{T_4}{T_3} = \left(\frac{V_3}{V_4}\right)^{\gamma-1} = \left(\frac{V_3}{V_1}\right)^{\gamma-1} = \left(\frac{\alpha}{\beta}\right)^{\gamma-1}$$

$$\frac{T_4}{T_1} = \frac{T_4}{T_3}\cdot\frac{T_3}{T_2}\cdot\frac{T_2}{T_1} = \alpha^{\gamma-1}\beta^{1-\gamma}\cdot\alpha\cdot\beta^{\gamma-1} = \alpha^\gamma$$

$$\eta = 1 - \gamma^{-1}\beta^{1-\gamma}\frac{\alpha^\gamma - 1}{\alpha - 1}.$$ 3'

$$-\frac{\partial\eta}{\partial\alpha} \sim (\gamma\alpha^{\gamma-1})(\alpha-1) - (\alpha^\gamma - 1) = \gamma\alpha^\gamma - \gamma\alpha^{\gamma-1} - \alpha^\gamma + 1$$

$$= (\gamma-1)\alpha^\gamma - \gamma\alpha^{\gamma-1} + 1$$

$$\equiv f[\alpha]$$

Note that

$f[1] = \gamma - 1 - \gamma + 1 = 0.$

$\partial f / \partial \alpha = \gamma(\gamma-1)\alpha^{\gamma-1} - \gamma(\gamma-1)\alpha^{\gamma-2}$

$- \gamma(\gamma-1)\alpha^{\gamma-2}(\alpha-1) > 0.$ for $\alpha > 1.$

3'

so that $f[\alpha] > 0$, i.e $\partial \eta / \partial \alpha < 0.$ 2'

$\frac{\partial \eta}{\partial \beta} \sim (\gamma - 1)\beta^{-\gamma} > 0.$ 2'