2024秋物理化学I第二次测验

1. Carnot 热机：$\eta = 1 - \frac{T_l}{T_h} < 1$

制冷机：$\eta = \frac{T_l}{T_h - T_l} > 1$ when $T_h - T_l < T_l$

所有两热源间可逆热机 $\eta = \eta_{Carnot}$ $\Rightarrow$ B.

2.

初态 $\xrightarrow[\Delta U=0,\ W=-Q]{\text{等温膨胀}}$ 末态

$|W_{max}| = 4Q$ 最大功：等温可逆膨胀

$Q' = -W_{max} = 4Q$，$\Delta S = \frac{Q'_{rev}}{T} = \frac{4Q}{T}$ $\Rightarrow$ A.

3. $đQ = đW = dU = 0$

$$\left.\begin{array}{l} TdS - pdV = 0,\ dV > 0 \Rightarrow dS > 0, \\ dG = -SdT + Vdp = Vdp \Rightarrow dG < 0 \end{array}\right\} \Rightarrow \text{D.}$$

4. $\Delta G = \Delta(A + pV) = \Delta A + nR\Delta T = \Delta A$ $\Rightarrow$ A.

5. $đQ = 0$. $đW = 0$：Joule 膨胀

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial T}{\partial U}\right)_V\left(\frac{\partial U}{\partial V}\right)_T = -\frac{1}{C_V}\left(\frac{T\partial S - p\partial V}{\partial V}\right)_T$$

$$= -\frac{1}{C_V}\left(T\left(\frac{\partial p}{\partial T}\right)_V - p\right), \quad p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$= -\frac{1}{C_V}\left(\frac{RT}{V_m - b} - p\right)$$

$$= -\frac{1}{C_V}\frac{a}{V_m^2} < 0 \Rightarrow \text{降低}$$

Joule-Thomson 过程 存在临界点，无法确定 $\Rightarrow$ A.

6.

$\Delta_r A_m^\ominus = \Delta_r (G - pV)_m^\ominus = \Delta_r G_m^\ominus - RT\Delta\nu$

$\Delta\nu = 2-3 = -1 < 0 \Rightarrow \Delta_r A_m^\ominus - \Delta_r G_m^\ominus > 0. \Rightarrow C.$

7. 考虑系统处于 T_0 的 bath 中，则对于 $đQ$ 热量变化，

$dS_{bath} = -\frac{đQ}{T_0}$

$dS + dS_{bath} \geq 0 \Rightarrow T_0 dS \geq đQ,$

while $dU = đQ + đW = đQ + đW_f - p_0 dV$

when $đW_f = 0 \Rightarrow$

$đQ = dU + p_0 dV \leq T_0 dS,$

$dU \leq T_0 dS - p_0 dV.$

$dS, dV = 0 \Rightarrow dU \leq 0.$

Similarly, $dp = 0 \Rightarrow p = p_0$,

$dH = dU + d(pV) \leq T_0 dS + V dp_0 = 0.$ $(dS)_{H,p} \geq 0.$

Similarly, $dT = 0 \Rightarrow T = T_0$,

$dA = dU - d(TS) \leq -S dT_0 - p_0 dV,$

$p_0 dV \leq -S dT_0 - dA = 0 \Rightarrow C.$

8. $C_V dT = dU = TdS - pdV$, $dT = 0, dV = 0 \Rightarrow dS = 0.$

$dH = C_p dT = 0 \Rightarrow A.$

9. 此时绝热过程为等温过程. $C_p/C_V = 1$. 自然无理想气体.

"不可有限手段使热力学温度达到绝对零度" $\Rightarrow D$

10.

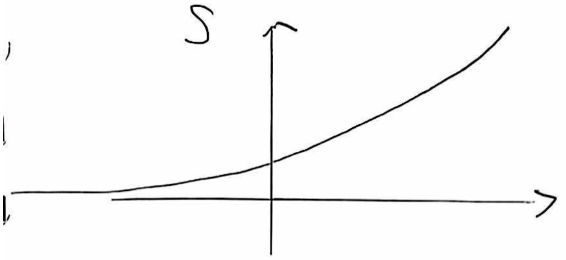
$$\text{LHS} = \frac{p\left(\partial G/\partial T\right)_p - G\left(\partial p/\partial T\right)_p}{p^2} = \frac{1}{p}\left(\frac{\partial G}{\partial T}\right)_p = \frac{1}{p}\left(\frac{-S\partial T + V\partial p}{\partial T}\right)_p$$

$$= -\frac{S}{p} = \text{RHS}.$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{T\partial S + \cancel{p\partial} V\partial p}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p,$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V,$$

其可统一表示 $\cancel{T}\left(\frac{\partial S}{\partial \ln T}\right)$:



对 $T \to 0$, $\ln T \to -\infty$, $S \to$ Const

$$\left(\frac{\partial S}{\partial \ln T}\right) = 0.$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{T\partial S - p\partial V}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p.$$

$$\text{LHS} = \frac{\partial}{\partial p}\left(T\left(\frac{\partial S}{\partial T}\right)_p\right)_T = T\frac{\partial}{\partial T}\left(\left(\frac{\partial S}{\partial p}\right)_T\right)_p + \left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_T$$

$$= T\frac{\partial}{\partial T}\left(-\left(\frac{\partial V}{\partial T}\right)_p\right)_p = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p \Rightarrow \text{D}.$$

~~11.~~ 12.

$$dH = TdS + Vdp \Rightarrow \left(\frac{\partial p}{\partial S}\right)_H = -\frac{T}{V} < 0,$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V > 0$$

product <0.

$dU = TdS - pdV$

$$\frac{\partial(p\ T)}{S\ T}\ \frac{S\ G}{V\ G}\ \frac{T\ S}{G\ S}\ \frac{G\ V}{T\ V}\ \cancel{\frac{H\ p}{S\ p}}\qquad \left(\frac{\partial V}{\partial U}\right)_S$$

$$= \left(\frac{\partial p}{\partial V}\right)_T\cancel{\left(\frac{\partial H}{\partial S}\right)_p} = -\frac{nRT}{V^2}, \xrightarrow{\text{product}} \frac{nRT}{V^2 p} > 0 \Rightarrow \text{B}.$$

$$\left(\frac{\partial H}{\partial S}\right)_V = \left(\frac{T\partial S + V\partial p}{\partial S}\right)_V = T + V\left(\frac{\partial p}{\partial S}\right)_V$$

$$-C = S\left(\frac{\partial T}{\partial S}\right)_V - V\left(\frac{\partial p}{\partial S}\right)_V$$

$$= S\left(\frac{\partial T}{\partial S}\right)_V - \left(\frac{\partial (pV)}{\partial S}\right)_V = S\left(\frac{\partial T}{\partial S}\right)_V - nR\left(\frac{\partial T}{\partial S}\right)_V$$

$$= \underbrace{(S-nR)}_{\text{unsure}}\underbrace{\left(\frac{\partial T}{\partial S}\right)_V}_{T/C_V > 0} \qquad \exists\, S-nR>0 \Rightarrow C<0.$$

$$\left(\frac{\partial A}{\partial p}\right)_T - \left(\frac{\partial U}{\partial p}\right)_T = \left(\frac{\partial (A-U)}{\partial p}\right)_T = -\left(\frac{\partial (TS)}{\partial p}\right)_T$$

$$= -T\left(\frac{\partial S}{\partial p}\right)_T = T\left(\frac{\partial V}{\partial T}\right)_p = V > 0 \Rightarrow D.$$

11.

$$dQ = dW = 0, \quad dU = 0 \Rightarrow dT = 0,$$

$$0 = TdS - pdV \Rightarrow dS = \frac{pdV}{T} = \frac{nR}{V}dV$$

$$\Delta S = \int \frac{nR}{V}dV = nR\ln\frac{dV}{d} = nR\ln\alpha. \Rightarrow A.$$

$$dT = 0 \Rightarrow dU = 0. \quad \Delta S = nR\ln\alpha.$$

van der Waals : $\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT. \quad p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$

vacuum: $dS = \frac{pdV}{T} \quad . \cancel{\left(\frac{\partial T}{\partial V}\right)_U} =$

Consider $S[T,V]$, $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

$$TdS = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV = pdV,$$

$$dT = \frac{1}{C_V}\left(p - T\left(\frac{\partial p}{\partial T}\right)_V\right)dV, \quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V_m - b}$$

$$= \frac{1}{C_V}\left(-\frac{a}{V_m^2}\right)dV = -\frac{an^2}{C_V}\frac{dV}{V^2}$$

$$\Delta T \propto \left(\frac{1}{\alpha V} - \frac{1}{V}\right) \propto \frac{\alpha - 1}{\alpha V} \propto \frac{\alpha - 1}{\alpha} \Rightarrow C.$$

Ideal gas: $dS = \frac{p}{T}dV = \frac{nR}{V}dV$. $\Delta S = nR\ln\alpha$,

vdW: $dU = TdS - pdV$

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

$$TdS = pdV + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{T\partial S - p\partial V}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

$$= T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$$TdS = T\left(\frac{\partial p}{\partial T}\right)_V dV, \qquad p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$dS = \frac{R}{V_m - b}dV = \frac{nR}{V - nb}dV > \frac{nR}{V}dV. \Rightarrow D.$$

13. $\left(\frac{\partial H}{\partial T}\right)_p = C_p \Rightarrow$

$$\Delta_r H_m^\ominus[T] - \Delta_r H_m^\ominus[T_0] = \int_{T_0}^{T} \Delta_r C_{p,m}^\ominus[T]dT, \quad 3'$$

$$\Delta_r H_m^\ominus = \int_{368.5}^{T} 0.356 + 2.76e\text{-}3\, T\, dT + 4.02$$

$$= 0.356(T - 368.5) + \frac{2.76e\text{-}3}{2}(T^2 - 368.5^2) + 4.02$$

$$= 1.38e\text{-}3\, T^2 + 0.356T + 83.42 \quad 3'$$

Gibbs-Helmholtz: 3'

$$\left(\frac{\partial \frac{\Delta_r G_m^\ominus}{T}}{\partial T}\right)_p = -\frac{\Delta_r H_m^\ominus}{T^2} = -83.42T^{-2} - 0.356T^{-1} - 1.38e\text{-}3.$$

$$\left(\Delta_r G_m^\ominus / T\right)[298.15] = \int_{368.5}^{298.15} -\frac{\Delta_r H_m^\ominus}{T^2}dT = 0.2259 > 0 \Rightarrow \text{斜方更稳定.}$$

3' 2' 1'

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(1) 双原子理想气体. $C_{V,m}=\frac{5}{2}R$. $C_{p,m}=\frac{7}{2}R$. $\gamma=7/5$, 1'

初态: 10^5 Pa, 298.15 K, 0.024790 m^3

末态. $pV^{\gamma}=\text{Const}$, $p=10^6$ Pa $\Rightarrow$ $V=4.1352e{-3}$. $T=497.35$ 1'

$\Delta U=C_V\Delta T=4140.621$. 2'

$Q=0$. 2'

$W=\Delta U=4140.621$, 2'

$\Delta H=C_p\Delta T=5796.869$. 2'

$\Delta S=\oint\frac{dQ_{rev}}{T}=0$, 2'

$\Delta S_{环境}=0$, 2'

$\Delta A=\Delta(U-TS)=\Delta U-S\Delta T=(C_V-S)\Delta T=-36723.267$. 2'

$\Delta G=(C_p-S)\Delta T=-35067.019$. 2'

(2) 末态: ~~$p=10^6$ $\Rightarrow$ $T=29.815$ K~~

$p=5e{+4}$ $\Rightarrow$ $T=596.3$ 1', $V=0.099159$. 1'

$pT=\text{Const}$ $\Rightarrow$ $d(pT)=0$.

$\frac{nR}{V}$

$C_V dT=TdS-pdV$, $dS=\frac{C_V}{T}dT+\frac{p}{T}dV$

$\Delta S=C_V\ln\frac{596.3}{298.15}+nR\ln\frac{0.99159}{0.24790}=25.934$. 3'

$\Delta A=C_V\Delta T-\Delta(TS)$

$=C_V\Delta T-\left(596.3(S_m^{\ominus}+\Delta S)-298.15S_m^{\ominus}\right)$

$=-70429.515$. 3'

15.

(1) $$C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial (U+pV)}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V$$ $1'$

$$= \left(\frac{\partial U}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V + p\left(\frac{\partial V}{\partial T}\right)_p$$ $2'$

$$= \left(\frac{\partial U}{\partial T}\right)_p - \left(\left(\frac{\partial U}{\partial T}\right)_p\left(\frac{\partial T}{\partial T}\right)_V + \left(\frac{\partial U}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_V\right) + p\left(\frac{\partial V}{\partial T}\right)_p$$

$$= -\left(\frac{\partial U}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_V + p\left(\frac{\partial V}{\partial T}\right)_p$$ $2'$

$$= -\left(\frac{T\partial S - p\partial V}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_V + p\left(\frac{\partial V}{\partial T}\right)_p$$ $2'$

$$= p\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_V + p\left(\frac{\partial V}{\partial T}\right)_p - T\left(\frac{\partial S}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_V$$

$$= T\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial p}{\partial T}\right)_V$$ $2'$

$$\frac{VT\beta_p^2}{K_T} = -\frac{T\left(\frac{\partial V}{\partial T}\right)_p^2}{\left(\frac{\partial V}{\partial p}\right)_T} = T\left(\frac{\partial V}{\partial T}\right)_p \frac{\partial(p,V)}{\partial(T,p)}\frac{\partial(T,p)}{\partial(T,V)} = \mathrm{LHS}$$ $2'$

(2) $$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{T\partial S - p\partial V}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$ $2'$

$$\frac{C_p - C_V}{V\beta_p} = \frac{T\beta_p}{K_T} = -T\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} = T\left(\frac{\partial p}{\partial T}\right)_V.$$ $2'$

(3). $$\lim_{T\to 0}\beta_p = \lim_{T\to 0} \cancel{\partial \ln V} -\frac{1}{V}\left(\frac{\partial S}{\partial p}\right)_T$$ $1'$

while $\lim_{T\to 0}\delta S = 0 \Rightarrow \lim_{T\to 0}\beta_p = 0.$ $2'$

$1'$