2. (1)

当 $\frac{m}{V_1}=4\ kg/m^3$ 时开始液化，有

$$V_1=\frac{0.027}{4}=6.75\times10^{-3}\ m^3$$

(2) $$V_2=\frac{0.027}{1.3\times10^3}=2.0769\times10^{-5}\ m^3$$

(3) 设气体体积为 V_1，液体体积为 V_2

$$\begin{cases} V_1+V_2=1\times10^{-3} \\ 4V_1+1.3\times10^3V_2=0.027 \end{cases}$$

得 $$\begin{cases} V_1=9.8225\times10^{-4}m^3 \\ V_2=1.775\times10^{-5}m^3 \end{cases}$$

7. 由克拉伯龙方程，得 $(PV=RT)$

$$\frac{dp}{dT}=\frac{\lambda}{T(V_2-V_1)}\approx\frac{\lambda P}{RT^2}$$

得 $$\ln P+C=-\frac{\lambda}{RT}$$

故有 $$\ln\frac{P_1}{P_2}=\frac{\lambda}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

得 $\lambda\approx 92.606\ J/mol$

18. 在恒温条件下，次姆赤赤兹自由能为

$$F(T,x)=F(T,0)-\int_0^x F'dx$$

而 $F'=-kx$

有 $F(T,x)=F(T,0)+\frac{1}{2}k(T)x^2$

而 $\left(\frac{\partial S}{\partial x}\right)_T=\left(\frac{\partial F'}{\partial T}\right)_x=-\frac{dk(T)}{dT}x$

故而 $S(T,x)=S(T,0)-\frac{1}{2}\frac{dk(T)}{dT}x^2$

$$\left(\frac{\partial U}{\partial x}\right)_T=T\left(\frac{\partial S}{\partial x}\right)_T+kx$$

$$=-T\frac{dk(T)}{dT}x+kx$$

故而 $U(T,x)=U(T,0)+\frac{1}{2}\left(k-T\frac{dk(T)}{dT}\right)x^2$

24. (1) 系统在可逆等温过程中，有

$$Q=T\Delta S$$

而 $\left(\frac{\partial S}{\partial H}\right)_T=V\mu_0\left(\frac{\partial M}{\partial T}\right)_H$

$$\left(\frac{\partial M}{\partial T}\right)_H = -\frac{C}{T^2}H$$

故而 $\left(\frac{\partial S}{\partial H}\right)_T = V\mu_0\left(-\frac{C}{T^2}H\right) = -\frac{VC\mu_0}{T^2}H$

$$\Delta S = \int_0^H \left(\frac{\partial S}{\partial H}\right)_T dH = -\frac{CV\mu_0 H^2}{T^2}$$

$$Q = T\Delta S = -\frac{CV\mu_0 H^2}{2T}$$

(2) $F(T,M) = F(T,0) + \int \mu_0 H dM = F(T,0) + \frac{\mu_0 T M^2}{2C}$

$$S(T,M) = -\frac{dF}{dT} = S(T,0) - \frac{\mu_0 M^2}{2C}$$

$$U = F + TS = F(T,0) + TS(T,0)$$

$$U = U(T,0)$$

26. $C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad C_v = \left(\frac{\partial U}{\partial T}\right)_V$

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

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

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

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

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

若 $\left(\frac{\partial p}{\partial V}\right)_T < 0$

则由 $\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial T}{\partial V}\right)_p = -1$

得 $\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p > 0$

故而 $C_p > 0$

而 $\left(\frac{\partial p}{\partial V}\right)_S = \left(\frac{\partial p}{\partial V}\right)_T + \left(\frac{\partial p}{\partial S}\right)_V\left(\frac{\partial S}{\partial V}\right)_T$

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

而 $\frac{1}{\left(\frac{\partial p}{\partial S}\right)_V} = \left(\frac{\partial S}{\partial p}\right)_V$

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

$$\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial p}{\partial S}\right)_V = \frac{1}{\frac{C_p}{T}\left(\frac{\partial T}{\partial p}\right)_V^2 - \left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_V}$$

有 $\frac{C_p}{T}\left(\frac{\partial T}{\partial p}\right)_V^2 - \left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_V < 0$

故而 $\left(\frac{\partial p}{\partial V}\right)_s < 0$

32. 相变潜热 $\lambda = h^\beta - h^\alpha$

而 $\frac{dh}{dT} = \left(\frac{\partial h}{\partial T}\right)_p + \left(\frac{\partial h}{\partial p}\right)_T \frac{dp}{dT}$

$$= c_p + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] \frac{dp}{dT}$$

由克拉珀龙方程，有

$$\frac{dp}{dT} = \frac{\lambda}{T(V_m^\beta - V_m^\alpha)}$$

故而 $\frac{dh}{dT} = C_p + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] \frac{\lambda}{T(V_m^\beta - V_m^\alpha)}$

进而 $\frac{d\lambda}{dT} = C_p^\beta - C_p^\alpha + \frac{\lambda}{T} + \left[\left(\frac{\partial V_m^\alpha}{\partial T}\right)_p - \left(\frac{\partial V_m^\beta}{\partial T}\right)_p\right] \frac{\lambda}{(V_m^\beta - V_m^\alpha)}$

当 β 相为气相，α 是液相时，

$$V_m^\beta \gg V_m^\alpha$$

且 $V_m^\beta \propto T$

故而 $\frac{\partial V_m^\beta}{\partial T} = \frac{V_m^\beta}{T}$

有 $\frac{d\lambda}{dT} = C_p^\beta - C_p^\alpha + \frac{\lambda}{T} - \frac{\lambda}{T} = C_p^\beta - C_p^\alpha$

33. $$d(pV_m) = d(RT)$$

$$V_m\,dp + p\,dV_m = R\,dT$$

$$V_m \frac{dp}{dT} + p\frac{dV_m}{dT} = R$$

$$p\frac{dV_m}{dT} = R - V_m\frac{dp}{dT} \approx R - V_m\frac{\lambda}{TV_m}$$

$$\frac{dV_m}{dT} = \frac{1}{p}\left(R - \frac{\lambda}{T}\right)$$

$$\frac{1}{V_m}\frac{dV_m}{dT} = \frac{1}{RT}\left(R - \frac{\lambda}{T}\right)$$

$$\frac{1}{V_m}\frac{dV_m}{dT} = \frac{1}{T}\left(1 - \frac{\lambda}{RT}\right)$$