Specific Heat

1) What is the specific heat (C_v) of an
1P) diatomic ideal gas? N, V, T (at large T)

$$U = \frac{f}{2} NkT$$


$f = 3$ transl. $+ 2 \times 1$ vibr. $+ 2$ rotat.

$$\rightarrow U = \frac{7}{2} NkT \quad \longrightarrow \quad C_v = \left(\frac{\partial U}{\partial T}\right)_V = \boxed{\frac{7}{2} Nk}$$

2) For this system
2P) What is ΔS if the temperature T_i is increased to T_f?

$$\Delta S = \int \frac{Q}{T} = \int_{T_i}^{T_f} \frac{C_v \, dT}{T} = \int_{T_i}^{T_f} \frac{\frac{7}{2} Nk \, dT}{T}$$

$$= \boxed{\frac{7}{2} Nk \ln\left(\frac{T_f}{T_i}\right)}$$

Thermodynamic Identities

$$dU = TdS - pdV + \mu dN$$

a) $dG = ?$ $\qquad G = U - TS + pV$

$$dG = dU - TdS - SdT + pdV + Vdp$$

$$= (\cancel{TdS} - \cancel{pdV} + \mu dN) - \cancel{TdS} - SdT + \cancel{pdV} + Vdp$$

$$= -SdT + Vdp + \mu dN$$

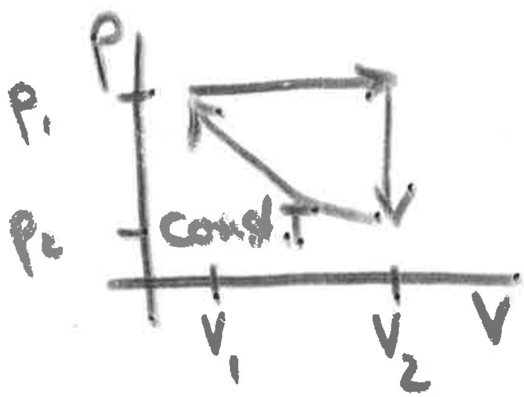
b) Maxwell relation: List two (there are more)

$$\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right) = \frac{\partial}{\partial T}\frac{\partial G}{\partial p} \rightarrow -\left(\frac{\partial S}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{p,N}$$

$$\frac{\partial}{\partial N}\frac{\partial G}{\partial T} = \frac{\partial}{\partial T}\frac{\partial G}{\partial N} \rightarrow -\left(\frac{\partial S}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial T}\right)_{p,N}$$

$$\frac{\partial}{\partial N}\frac{\partial G}{\partial p} = \frac{\partial}{\partial p}\frac{\partial G}{\partial N} \rightarrow \left(\frac{\partial V}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial p}\right)_{T,N}$$

1st Law of Therm. & Heat Engines & Refridg.

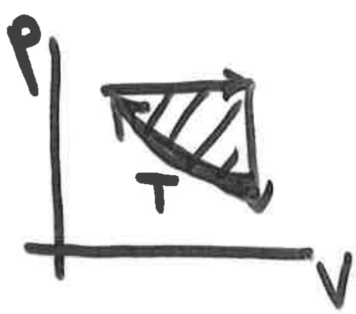


ideal diatomic gas at high T

Determine $\varepsilon = \frac{W_{by}}{Q_h}$

a) W_{by} b) Q_h

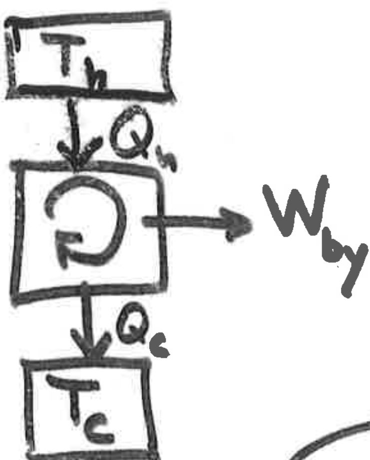
$\varepsilon = \frac{W_{by}}{Q_h}$



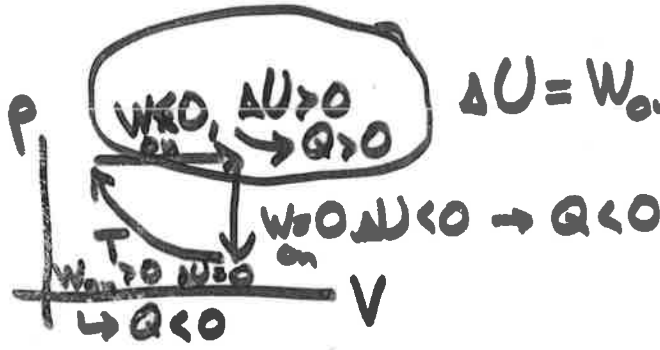
a) $W_{by} = +\oint p\,dV$

$= p_1(V_2 - V_1) + \int_{V_2}^{V_1} \frac{NkT}{V}\,dV$

$= p_1(V_2 - V_1) + p_1V_1 \ln\frac{V_1}{V_2}$



b)



$\Delta U = W_{on} + Q$

$Q_h = \Delta U - W_{on} = \frac{7}{2}Nk\,\Delta T + \int_{V_1}^{V_2} p\,dV$

O~O

$f =$ 3 trans + 2 × 1 vibr. + 2 rot.

$Q_h = \frac{7}{2}p_1(V_2 - V_1) + p_1(V_2 - V_1)$

$= \frac{9}{2}p_1(V_2 - V_1)$

Multiplicities & Entropy

a) What is Ω for an Einstein solid?

$$\Omega(q,N) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!\,(N-1)!} \approx \frac{(q+N)!}{q!\,N!}$$

$\bullet\bullet\bullet|\bullet|\bullet\bullet|\bullet\bullet\bullet$

b) Approximate $\Omega(q,N)$ $\boxed{\overbrace{\text{for } q \gg N}^{c)} \quad (\text{high } T) \quad \& \; q, N \gg 1}$

b) $$\ln\Omega = \ln(q+N)! - \ln q! - \ln N!$$

$$\overset{\text{Stirling}}{\approx} (q+N)\ln(q+N) - (q+N) - [q\ln q - q] - \{N\ln N - N$$

$$= (q+N)\ln(q+N) - q\ln q - N\ln N$$

c) $$= (q+N)\left[\ln q + \ln\left(1+\frac{N}{q}\right)\right] - q\ln q - N\ln N$$

$$\approx \cancel{q\ln q} + N\ln q + \underbrace{(q+N)}_{}\left(\frac{N}{q}\right) - \cancel{q\ln q} - N\ln N$$

$\rightarrow 0$

$$= N\ln\frac{qe}{N}$$

$$\Omega \approx \left(\frac{qe}{N}\right)^N$$

d) Using this result $\Omega = \left(\frac{q\epsilon}{N}\right)^N$ and $U = q\varepsilon$ determine $U(T)$.

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{\partial}{\partial U}\left[k \ln\left(\frac{q e}{N}\right)^N\right] = \frac{\partial}{\partial U}\left[Nk \ln\left(\frac{U e}{\varepsilon N}\right)\right]$$

$$= Nk \frac{1}{U}$$

$\rightarrow$ $U = NkT$ (consistent with equipart. thm)

Phase Transitions

For the Van der Waals Model

$$p = \frac{NkT}{(V-Nb)} - a\frac{N^2}{V^2}$$

One (you could) can show that $V_c = 3Nb$.

Determine kT_c (as function of a & b only!)

Critical point: $\frac{\partial p}{\partial V} = 0$ & $\frac{\partial^2 p}{\partial V^2} = 0$

at $T = T_c$

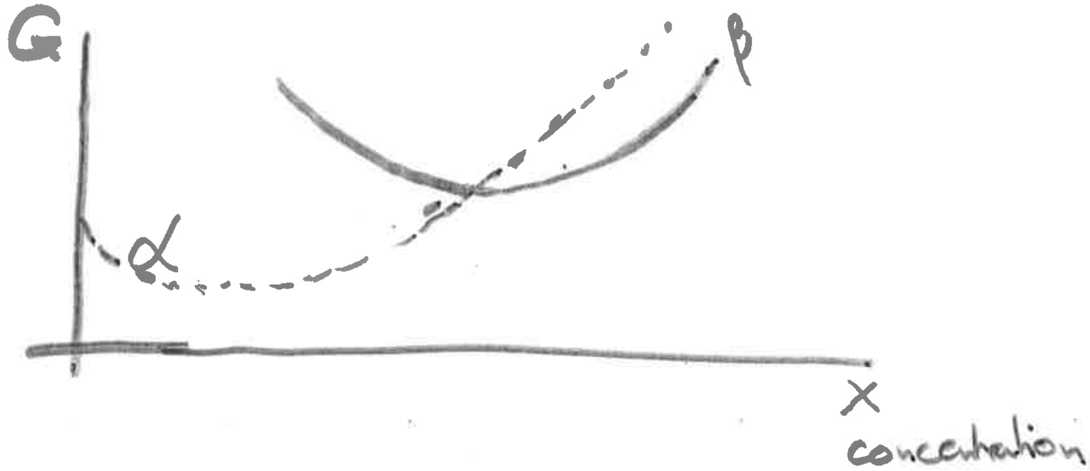
$$-\frac{NkT}{(V-Nb)^2} + \frac{2aN^2}{V^3} = 0$$

$$\rightarrow kT_c = \frac{2aN^2}{V_c^3}\frac{(V_c - Nb)^2}{N} = \frac{2a\cancel{N^2}}{(3\cancel{N}b)^3}\frac{(2\cancel{N}b)^2}{\cancel{N}}$$

$$= \boxed{\frac{8}{27}\frac{a}{b}}$$

PhaseTransitions / Phase Separation

For the following scenario:



Is there phase separation? For which x-range?
If yes into which to phases
does the system separate?