

## Simple Steps

$$a) \quad P_i = \frac{e^{-\beta E_i}}{Z}$$

$$\begin{aligned} \frac{S}{k_B} &= - \sum_i P_i \ln P_i \\ &= - \sum_i \frac{e^{-\beta E_i}}{Z} \ln \frac{e^{-\beta E_i}}{Z} \end{aligned}$$

$$= - \sum_i \frac{e^{-\beta E_i}}{Z} (-\beta E_i) + \sum_i \frac{e^{-\beta E_i}}{Z} \ln Z$$

$$= \frac{\sum_i e^{-\beta E_i} (-\beta E_i)}{Z} + \ln Z \sum_i \frac{e^{-\beta E_i}}{Z}$$

$$\boxed{\frac{S}{k_B} = \beta \bar{E} + \ln Z}$$

$$\text{So } \ln Z = \frac{S}{k_B} - \frac{\bar{E}}{k_B T} = -\frac{F}{k_B T}$$

And

$$\boxed{Z = e^{-F/k_B T}}$$

$$b) \quad dU = TdS - pdV$$

$$d(U - TS) = TdS - pdV - (TdS + SdT)$$

$$F \equiv U - TS \quad dF = -SdT - pdV$$

$$d(F + pV) = -SdT - pdV + (pdV + Vdp)$$

$$G = U - TS + pV$$

$$dG = -SdT + Vdp$$

$$c) \quad S_0$$

$$-T^2 \left( \frac{\partial (F/T)}{\partial T} \right)_V = F - \left( T \frac{\partial F}{\partial T} \right)_V = F + TS$$

we used  $dF = -SdT - pdV$ . Then since  $F = U - TS$ , we have

$$i) \quad -T^2 \frac{\partial (F/T)}{\partial T} = U \quad \checkmark$$

$$ii) \quad C_V = T \left( \frac{\partial S}{\partial T} \right)_V = -T \frac{\partial}{\partial T} \left( \frac{\partial F}{\partial T} \right)_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V \quad \checkmark$$

iii)

$$-T^2 \left( \frac{\partial (G/T)}{\partial T} \right)_P = G - T \left( \frac{\partial G}{\partial T} \right)_P = G - T(-S) = G + TS$$



But  $G = U - TS + pV$  and  $H = U + pV$  and so

$$-T^2 \left( \frac{\partial (G/T)}{\partial T} \right)_p = H \quad \checkmark$$

So

$$C_p = T \left( \frac{\partial S}{\partial T} \right)_p = T \left( \frac{\partial}{\partial T} \right)_p \cdot \left( \frac{\partial G}{\partial T} \right)_p = T \left( \frac{\partial^2 G}{\partial T^2} \right)_p \quad \checkmark$$

## Vander Wall

$$pV = RT \left( 1 + \frac{B}{V} + \dots \right)$$

So the Volume is approximately given by:

$$V^{(0)} = \frac{RT}{p} = \frac{(8.32 \frac{\text{J}}{\text{mol} \cdot \text{K}}) (200^\circ \text{K})}{1 \text{ bar}} \quad 1 \text{ bar} \approx 1 \text{ atm} = 10^5 \frac{\text{N}}{\text{m}^2}$$

$$= 0.0166 \text{ m}^3 \quad \text{or } 16.6 \text{ L}$$

Then the  $B/V$  term corrects 1 by  $B/V$

$$p = \frac{RT}{V^{(0)}} \left( 1 + \frac{B}{V} \right) = p_{\text{IG}} + \delta p$$

So

$$\frac{\delta p}{p_{\text{IG}}} = \frac{B/V}{p_{\text{IG}}} = \frac{-35 \text{ cm}^3}{0.0166 \text{ m}^3} = -0.2\% \quad \text{We expect the } C \text{ terms of order } (0.2\%)^2.$$

b) Well at low temperatures the gas should liquefy. the forces are attractive at large distances so we want  $B < 0$  at low temperature. At high temperature the forces are repulsive the molecules bounce off each other. So we expect  $B > 0$  at high temperatures

$$\begin{aligned} c) \quad P &= \frac{RT}{V-b} - \frac{a}{V^2} \approx \frac{RT}{V} \left( 1 + \frac{b}{V} + \left( \frac{b}{V} \right)^2 \right) - \frac{a}{V^2} \\ &\approx \frac{RT}{V} \left( 1 + \frac{b - a/RT}{V} + \frac{b^2}{V^2} + \dots \right) \end{aligned}$$



So comparison gives  $P = RT/V \left( 1 + \frac{B(T)}{V} + \frac{C}{V^2} \right)$

$$B(T) = b - \frac{a}{RT}$$

$$C = b^2$$

d) See figure in homework.

## Energy in van der Waals

We need the first and second  $TdS$  equations

$$TdS = C_v dT + T \left( \frac{\partial p}{\partial T} \right)_v dV \quad \text{first}$$

$$TdS = C_p dT - T \left( \frac{\partial V}{\partial T} \right)_p dp \quad \text{second}$$

The first expresses  $dS$  in terms of  $T, V$  while the second in  $T, p$ . Note both  $\left( \frac{\partial p}{\partial T} \right)_v$  and  $\left( \frac{\partial V}{\partial T} \right)_p$  can be expressed in terms of observables, e.g.

$$\beta_p \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \equiv \text{expansion coefficient}$$

• So using the first Law

$$dU = TdS - pdV$$

• and the first  $TdS$  equation

$$dU = C_v dT + \left[ T \left( \frac{\partial p}{\partial T} \right)_v - p \right] dV$$

So at fixed  $U$ ,  $dU = 0$  and  $\left. \frac{dT}{dV} \right|_{U=\text{fixed}} = -\frac{1}{C_v} \left( T \left( \frac{\partial p}{\partial T} \right)_v - p \right)$



i.e.

$$\left( \frac{\partial T}{\partial V} \right)_u = \frac{-1}{C_V} \left( T \left( \frac{\partial p}{\partial T} \right)_V - p \right)$$

• So we have

$$u = cRT - \frac{a}{V} \quad \text{so} \quad du = cR dT + \frac{a}{V^2} dV$$

So at fixed  $u$ ,  $du = 0$  and

$$\left( \frac{\partial T}{\partial V} \right)_u = \left. \frac{dT}{dV} \right|_{u \text{ fixed}} = - \frac{a}{cRV^2} \quad \leftarrow \text{this is the LHS of part a)}$$

while the RHS involves

$$p = \frac{RT}{b-V} - \frac{a}{V^2} \Rightarrow T \left( \frac{\partial p}{\partial T} \right)_V = \frac{RT}{b-V} \quad \text{and}$$

And so

$$T \left( \frac{\partial p}{\partial T} \right)_V - p = \frac{a}{V^2}$$

Then

$$C_V = \left( \frac{\partial u}{\partial T} \right)_V = cR$$

this is the RHS of (a)

So

$$\left[ -\frac{1}{C_V} \left[ T \left( \frac{\partial p}{\partial T} \right)_V - p \right] \right] = -\frac{1}{cR} \frac{a^2}{V^2}$$

this agrees with the boxed formula above confirming the formula from part (a)

(C) We have from the first TdS equation

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

So at fixed  $S$ ,  $dS = 0$  and

$$\left( \frac{\partial T}{\partial V} \right)_S = \left. \frac{dT}{dV} \right|_{S \text{ fixed}} = - \frac{1}{C_V} \left[ T \left( \frac{\partial p}{\partial T} \right)_V \right]$$

• Now for an ideal gas  $pV = NkT$ ,  $\left( \frac{\partial p}{\partial T} \right)_V = \frac{Nk}{V}$   
So

$$\left( \frac{\partial T}{\partial V} \right)_S = - \frac{1}{C_V} \frac{NkT}{V}$$

• Note for an ideal gas  $C_P = C_V + Nk$ , so  
 $Nk/C_V = \frac{C_P}{C_V} - 1 = \gamma - 1$ . Thus

$$\left( \frac{\partial T}{\partial V} \right)_S = - \frac{\gamma - 1}{V} T$$

• So at fixed entropy

$$\frac{dT}{T} = - \gamma - 1 \frac{dV}{V}, \text{ integrating both sides}$$



• we have

$$\ln T = -(\gamma - 1) \ln V + \text{const}$$

or

$$T = \frac{\text{const}}{V^{\gamma-1}} \quad \text{i.e.,} \quad TV^{\gamma-1} = \text{const}$$

• this implies,  $pV \propto T$ , so that

$$pV \cdot V^{\gamma-1} = \text{const} \quad \text{or}$$

$$\boxed{pV^{\gamma} = \text{const}}$$

## Temperature Change during free expansion

- We are considering a gas increasing its volume at fixed energy. We replace the non-equilibrium process with an equilibrium one

$$T_f - T_i = \int_i^f \left( \frac{\partial T}{\partial V} \right)_u dV$$

$$= \int_i^f -\frac{a}{cR V^2} dV$$

this is from problem 3.

$$= +\frac{a}{cR} \left( \frac{1}{V} \right) \Big|_i^f = \frac{a}{cR} \left( \frac{1}{V_f} - \frac{1}{V_i} \right)$$

Now  $V_f = \alpha V_i$  so we find

$$\boxed{T_f - T_i = -\frac{a}{cR V_i} \left( \frac{\alpha - 1}{\alpha} \right)}$$

Plugging numbers with  $\alpha = 5L/2L$  and  $a = 0.132 \text{ Pa m}^6$   
we have with  $V_i = 0.002 \text{ m}^3$ ,  $c = 1.5$ ,  $R = 8.32 \text{ J/K}$

$$\Delta T = -3.2 \text{ K}$$



Now for the entropy change we have

$$T dS = \frac{C_v}{T} dT + \left( \frac{\partial p}{\partial T} \right) dV$$

Then

$$C_v = \left( \frac{\partial u}{\partial T} \right)_v = CR$$

So

$$S_f - S_i = \int_{T_i}^T \frac{CR}{T} dT + \int_{V_i}^{V_f} \frac{R}{V-b} dV$$

$$\approx \frac{CR}{T_i} \Delta T + R \ln(V-b) \Big|_{V_i}^{V_f}$$

$$= \frac{CR}{T_i} \left( \frac{-a}{CR V_i} \right) \left( \frac{\alpha - 1}{\alpha} \right) + R \ln \left( \frac{V_f - b}{V_i - b} \right)$$

↑  
previous problem

$$S_f - S_i = \frac{-a}{T_i V_i} \left( \frac{\alpha - 1}{\alpha} \right) + R \ln \left( \frac{\alpha V - b}{V - b} \right)$$

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