

1. 2.00 L of an ideal gas at 10.00 bar expands isothermally to a final volume of 5.00 L at 4.00 bar.

[9] a) Calculate q , w , ΔU and ΔH if

i) the expansion is reversible ($p_{\text{external}} = p$)

ii) the expansion is irreversible with $p_{\text{external}} = 4.00$ bar

b) Explain how the results from part a illustrate that the internal energy and enthalpy are state functions, but work and heat are not.

2. Use the thermodynamic equation of state $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$

[2] to prove $(\partial U/\partial V)_T = 0$ for a gas obeying the equation of state

$$p = \frac{RT}{V_m - b}$$

3. 2.00 moles of a gas obeying the equation of state $p = \frac{RT}{V_m - b}$ with $b = 0.012$ L mol⁻¹

[5] expands reversibly and isothermally from 0.200 L and 283 bar to 1.50 L and 33.8 bar at 300 K.

a) Calculate q , w , ΔU and ΔH .

b) Do repulsive forces represented by the van der Waals b coefficient increase or decrease the work the expanding gas does on the surroundings? Explain briefly.

The following integral may be used to answer this question:

$$\int_{V_{m1}}^{V_{m2}} \frac{1}{V_m - b} dV_m = \ln\left(\frac{V_{m2} - b}{V_{m1} - b}\right)$$

4. a) Is $(\partial U/\partial V)_T$ an extensive property or an intensive property? Briefly justify your answer.

[2] b) Give the SI units of $(\partial U/\partial V)_T$.

5. If the only work performed is compression/expansion work and the pressure is constant, prove $\Delta H = q$. Why is this a useful result?

Chem 231

Assignment #2

(2016)

Q1 2.00 L

a) i 10.00 bar

reversible
expansion $(p = p_{\text{ext}})$

5.00 L

4.00 bar

isothermal ideal gas $dU = C_V dT = 0$

$$\Delta U = 0$$

$$w = -\int p_{\text{ext}} dV = -\int p dV \quad (\text{reversible})$$

$$= -\int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} \quad (\text{isothermal})$$

$nRT = p_i V_i = p_f V_f$

$$= -nRT \ln\left(\frac{V_f}{V_i}\right) = -p_i V_i \ln\left(\frac{V_f}{V_i}\right)$$

$$= -(10.00 \text{ bar}) \left(\frac{10^5 \text{ Pa}}{\text{bar}}\right) (2.00 \text{ L}) \left(\frac{10^{-3} \text{ m}^3}{\text{L}}\right) \ln\left(\frac{5.00 \text{ L}}{2.00 \text{ L}}\right)$$

$$w = -1832 \text{ J}$$

$$q = 1832 \text{ J}$$

$$\Delta U = q + w = 0$$

$$q = -w$$

$$\Delta H = H_f - H_i$$

$$(H = U + pV)$$

$$= U_f + p_f V_f - U_i - p_i V_i = \Delta U + p_f V_f - p_i V_i$$

$$= \Delta U + nRT_f - nRT_i = \Delta U + nR \Delta T \quad (\text{isothermal})$$

$$\Delta H = 0$$

or // use $dH = C_p dT$ (ideal gas)

$$dH = C_p dT \quad (\text{isothermal})$$

$$dH = 0$$

(Q1 cont.)

a) ii) 2.00 L $\xrightarrow{\text{irreversible expansion}}$ 5.00 L
10.00 bar $P_{\text{ext}} = 4.00 \text{ bar}$ 4.00 bar

$\Delta U = 0$
$\Delta H = 0$

isothermal ideal gas

$$w = - \int_{V_i}^{V_f} P_{\text{ext}} dV = - P_{\text{ext}} \int_{V_i}^{V_f} dV \quad (\text{constant } P_{\text{ext}})$$

$$= - P_{\text{ext}} (V_f - V_i)$$

$$= - (4.00 \text{ bar}) (5.00 \text{ L} - 2.00 \text{ L})$$

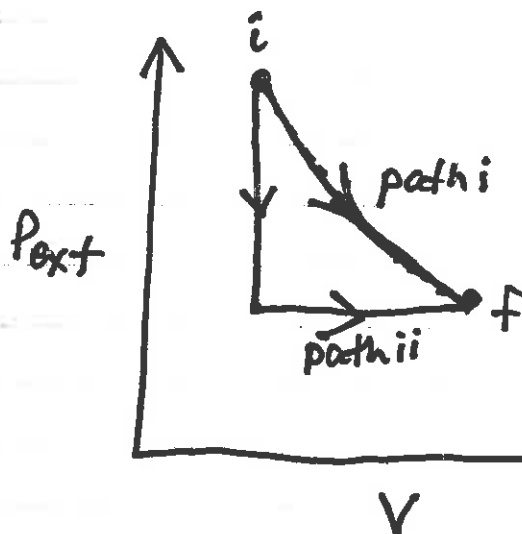
$$= -12.00 \text{ L bar} \left(10^{-3} \frac{\text{m}^3}{\text{L}} \right) \left(10^5 \frac{\text{Pa}}{\text{bar}} \right)$$

$$= -1200 \text{ m}^3 \text{ Pa}$$

$w = -1200 \text{ J}$
$q = 1200 \text{ J}$

$$\Delta U = 0 = q + w$$
$$q = -w$$

b)



$$\left\{ \begin{array}{l} \Delta U_{\text{path i}} = \Delta U_{\text{path ii}} = 0 \\ \Delta H_{\text{path i}} = \Delta H_{\text{path ii}} = 0 \end{array} \right\}$$

path independent

$$\left\{ \begin{array}{l} q_{\text{path i}} > q_{\text{path ii}} \\ w_{\text{path i}} < w_{\text{path ii}} \end{array} \right\}$$

path dependent

$P = \frac{RT}{V_m - b}$

Q2 $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$

(R, V_m, b)
constant

$= T \left(\frac{\partial}{\partial T} \frac{RT}{V_m - b}\right)_V - P$

= 1

$= T \frac{R}{V_m - b} \left(\frac{\partial T}{\partial T}\right)_V - \left(\frac{RT}{V_m - b}\right)$

$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V_m - b} - \frac{RT}{V_m - b} = 0$

Q3 $P = \frac{RT}{V_m - b} = \frac{RT}{\frac{V}{n} - b} = \frac{nRT}{V - nb}$

2.00 moles of gas expands reversibly ($p = P_{ext}$) and isothermally (300 K)

0.200 L $\xrightarrow{\text{rev.}}$ 1.50 L
283 bar 33.8 bar

work per mol

$\rightarrow W_m = - \int P_{ext} dV_m = - \int P dV_m$ (reversible)

$= - \int \frac{RT}{V_m - b} dV_m = - RT \int_{V_{mi}}^{V_{mf}} \frac{dV_m}{V_m - b} = - RT \ln \left(\frac{V_{mf} - b}{V_{mi} - b} \right)$

$W_m = - \left(\frac{8.314 \text{ J}}{\text{K mol}} \right) (300 \text{ K}) \ln \left[\frac{(0.750 - 0.012) \text{ L mol}^{-1}}{(0.100 - 0.012) \text{ L mol}^{-1}} \right]$

$W_m = -5304 \frac{\text{J}}{\text{mol}}$ $W = -10610 \text{ J}$ (see Q2) (for two moles of gas)

$\Delta U = \int_{V_i}^{V_f} \left(\frac{\partial U}{\partial V}\right)_T dT = \int (0) dT = 0$

$\Delta U = 0$
 $q = 10610 \text{ J}$

$q = -W$

(3 a) cont.)

$$\begin{aligned}\Delta H &= H_f - H_i = U_f + P_f V_f - (U_i + P_i V_i) \\ &= U_f - U_i + P_f V_f - P_i V_i = \cancel{\Delta U} + \Delta(PV) \\ &= P_f V_f - P_i V_i \\ &= (33.8 \text{ bar})(1.50 \text{ L}) - (283 \text{ bar})(0.200 \text{ L}) = -5.9 \text{ L bar}\end{aligned}$$

$$\boxed{\Delta H = -590 \text{ J}} \quad (1 \text{ L bar} = 100 \text{ J})$$

b) expand the gas from 0.200 L to 1.50 L at 300 K:

$$w_m = -RT \ln \left(\frac{V_{mf} - b}{V_{mi} - b} \right) = -5304 \text{ J}$$

gas is not ideal
 $b = 0.012 \text{ L mol}^{-1}$

expand an ideal gas from 0.200 L to 1.50 L at 300 K:

$$w_{m, \text{ideal}} = -RT \ln \frac{V_{mf}}{V_{mi}} = - \left(8.314 \frac{\text{J}}{\text{K mol}} \right) (300 \text{ K}) \ln \left(\frac{0.75}{0.100} \right)$$

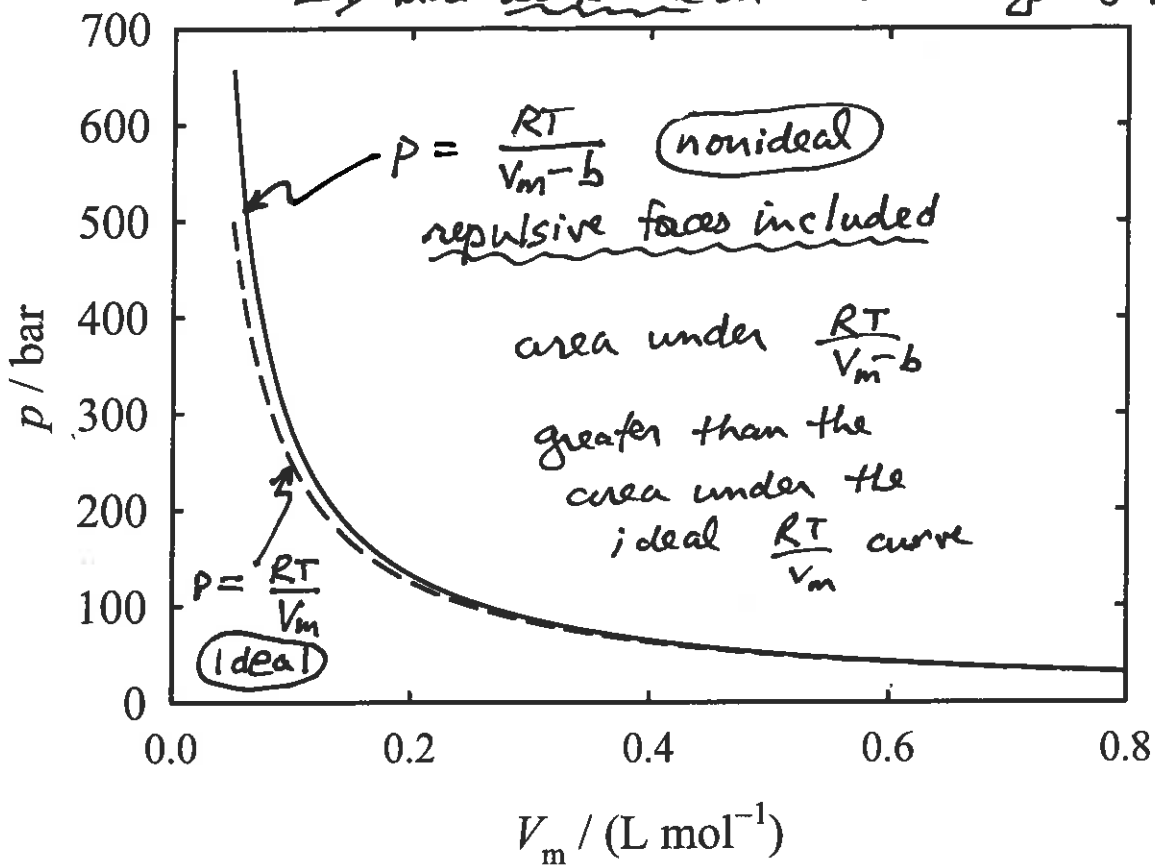
$$w_m = -5025 \text{ J mol}^{-1} \text{ if ideal}$$

the ideal gas does 5025 J mol⁻¹ on the surroundings,
the nonideal gas with repulsive parameter $b = 0.012 \frac{\text{L}}{\text{mol}}$
does 5304 J mol⁻¹ on the surroundings

nonideal gas molecules with repulsive forces do
more work on the surroundings when expanding
and "pushing each other apart".

(Q3) b)

repulsive forces indicated by
the van der Waals b parameter
 \Rightarrow more work done on surroundings by expanding gas



Q4

$$\left(\frac{\partial U}{\partial V}\right)_T$$

size independent
intensive or extensive?

size-dependent system property

from the thermodynamic equation of state:

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

notice that $(\partial U/\partial V)_T$ has the same units as pressure, an intensive system property

$\Rightarrow \therefore (\partial U/\partial V)_T$ is intensive

or use $\left(\frac{\partial U}{\partial V}\right)_T \approx \frac{\Delta U \leftarrow \text{extensive}}{\Delta V \leftarrow \text{extensive}}$ at constant temperature

an extensive property (U) divided by another extensive property (V) is intensive (size effect in the numerator cancels the size effect in the denominator)
(as in density = mass/volume)
(intensive)

b) SI units of $(\partial U/\partial V)_T$ are the SI units of pressure: $\boxed{\text{Pa}}$

Q5

Enthalpy H is defined as $U + pV$

$$dH = d(U + pV) = dU + d(pV) = dU + p dV + V dp$$

at constant pressure ($dp = 0$): $dH_p = dU_p + p dV_p + V dp$

$$dH_p = dU_p + p dV_p = dq_p + dw_p + p dV_p = dq_p - p dV_p + p dV_p$$

(only pV work)

$dH_p = dq_p \Rightarrow \boxed{\Delta H_p = q_p}$ allows calorimetric heat measurements to give ΔH data