

PHYS 5130 Problem Set 2 Solution

1. **Solution:** To treat this problem, one should note that the problem concerns an ideal gas, which has the following properties.

- Equation of state: $pV = NkT$
- Internal energy as a function of temperature only: $U = U(T)$.

As all three processes concerned have the same endpoints state 1 and state 2, which share the same temperature T_1 and so the same amount of internal energy, the overall change ΔU after each process is 0. Moreover, as $\Delta U = Q + W = 0$, $Q = -W$, so overall work done by the system ($-W$) equals overall heat flow into the system.

- (a) As the process is isothermal, throughout the process, the system has temperature T_1 . The work done to the system is given by

$$W = \int -pdV \quad (1)$$

$$= \int_{V_1}^{V_2} -\frac{nRT_1}{V} dV \quad (2)$$

$$= -nRT_1 \ln \frac{V_2}{V_1} \quad (3)$$

$$(4)$$

So the work done by the system is $nRT_1 \ln \frac{V_2}{V_1}$, which is also the heat flow into the system.

- (b) For the second path, it consists of path B, which is an adiabatic process, and path C, in which no work is done. For the adiabatic process, there is no heat exchange. Work done to the system is given by

$$W = \int -pdV \quad (5)$$

$$= - \int_{V_1}^{V_2} P_1 V_1^\gamma V^{-\gamma} dV \quad (6)$$

$$= -\frac{P_1 V_1^\gamma}{1-\gamma} (V_2^{1-\gamma} - V_1^{1-\gamma}) \quad (7)$$

$$= \frac{P_1 V_1}{\gamma-1} \left(\left(\frac{V_2}{V_1} \right)^{1-\gamma} - 1 \right) \quad (8)$$

For path C, there is no work done, but there is heat exchange, so that the overall $\Delta U = 0$. For the whole process, $Q = -W = -\frac{P_1 V_1}{\gamma-1} \left(\left(\frac{V_2}{V_1} \right)^{1-\gamma} - 1 \right)$

- (c) For path D, the work done to the system is simply given by $-P_1(V_2 - V_1)$, and for path E, there is no work done. So the overall work done by the system and heat flow into the system is $-W = P_1(V_2 - V_1) = Q$.

2. **Solution:** The equation of state for van der Waals equation of state is given by

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT \quad (9)$$

Rearranging the equation, one could obtain

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \quad (10)$$

Under an isothermal condition, temperature is a constant. Work done by the system is given by

$$-W = \int p dV \quad (11)$$

$$= \int_{V_1}^{V_2} \left(\frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \right) dV \quad (12)$$

$$= \left(nRT \ln(V - nb) + \frac{n^2 a}{V} \right) \Big|_{V_1}^{V_2} \quad (13)$$

$$= nRT \ln \left(\frac{V_2 - nb}{V_1 - nb} \right) + n^2 a (V_2^{-1} - V_1^{-1}) \quad (14)$$

Comparing the ideal gas law and the van der Waals equation, one could observe that when both a and b become 0, the van der Waals equation becomes the ideal gas law. So, when both a and b are 0, the same result for work done $nRT \ln \left(\frac{V_2}{V_1} \right)$ as ideal gas is obtained.

3. **Solution:** In this question, the slope $\left(\frac{\partial P}{\partial V} \right)$ of an isotherm and an adiabat are considered. For an isotherm,

$$pV = nRT. \quad (15)$$

$$\left(\frac{\partial PV}{\partial V} \right)_T = \left(\frac{\partial nRT}{\partial V} \right)_T \quad (16)$$

$$\left(\frac{\partial P}{\partial V} \right)_T V + P = 0 \quad (17)$$

$$\left(\frac{\partial P}{\partial V} \right)_T = -\frac{P}{V} \quad (18)$$

As both p and V are always positive, $\frac{\partial P}{\partial V}$ is negative, so as expected, when volume increases the pressure decreases (generally). For an adiabat,

$$PV^\gamma = C. \quad (19)$$

$$\left(\frac{\partial PV^\gamma}{\partial V} \right)_C = \left(\frac{\partial C}{\partial V} \right)_C \quad (20)$$

$$\gamma PV^{\gamma-1} + \left(\frac{\partial P}{\partial V} \right)_C V^\gamma = 0 \quad (21)$$

$$\left(\frac{\partial P}{\partial V} \right)_C = \frac{-\gamma P}{V} \quad (22)$$

Therefore, one also need to know the value of γ , which is determined by the species of the particles (Specific Heat Capacity / D.o.F) composing the gas. As $\gamma > 1$, an adiabat is steeper than an isothermal.

4. **Solution:** For one mole of monatomic ideal gas, internal energy is given by $\frac{3}{2}RT$, so one only needs to find the temperature to calculate ΔU . As $T = \frac{PV}{R}$,

$$\Delta U = \frac{3}{2}R(T_f - T_i) \quad (23)$$

$$= \frac{3}{2}P(V_f - V_i) \quad (24)$$

$$= 759 \text{ kJ} \quad (25)$$

Alternatively, as the process is isobaric so $Q = Q_p = C_p \Delta T$, $W = -p \Delta V$, where C_p is molar specific heat capacity.

Then,

$$\Delta U = Q + W \quad (26)$$

$$= C_p \Delta T - p \Delta V \quad (27)$$

$$= \frac{5}{2} R \Delta T - p \Delta V \quad (28)$$

$$= \frac{5}{2} p \Delta V - p \Delta V \quad (29)$$

$$= \frac{3}{2} p (V_f - V_i) \quad (30)$$

$$= 759 \text{ kJ} \quad (31)$$

5. **Solution:** As $nN_A = N$, one could first rewrite the van der Waal equation into

$$\left(p + \frac{N^2 a}{N_A^2 V^2} \right) \left(V - \frac{Nb}{N_A} \right) = NkT \quad (32)$$

$$\left(p + \frac{\tilde{n}^2 a}{N_A^2} \right) \left(\tilde{n}^{-1} - \frac{b}{N_A} \right) = kT \quad (33)$$

After expanding the terms and some rearrangement, one could arrive at

$$\frac{p}{kT} = \left(\tilde{n}^{-1} - \frac{b}{N_A} \right)^{-1} - \frac{\tilde{n}^2 a}{N_A^2 kT} \quad (34)$$

$$= \tilde{n} \left(1 - \frac{\tilde{n}b}{N_A} \right)^{-1} - \frac{\tilde{n}^2 a}{N_A^2 kT} \quad (35)$$

As van der Waals gas is a ‘correction’ to ideal gas in describing real gas, it can be expected that it is applicable to ‘relatively dilute’ gas, so $\frac{\tilde{n}b}{N_A} \ll 1$. Therefore, to first order, $\left(1 - \frac{\tilde{n}b}{N_A} \right)^{-1} \approx 1 + \frac{\tilde{n}b}{N_A}$. Then,

$$\frac{p}{kT} \approx \tilde{n} \left(1 + \frac{\tilde{n}b}{N_A} \right) - \frac{\tilde{n}^2 a}{N_A^2 kT} \quad (36)$$

$$= \tilde{n} + \tilde{n}^2 \left(\frac{b}{N_A} - \frac{a}{N_A^2 kT} \right). \quad (37)$$

One could then identify the second virial coefficient $B_2 = \frac{b}{N_A} - \frac{a}{N_A^2 kT}$. Here a arises due to the attraction between gas molecules, and b arises due to non-zero volume of the molecules. Whereas the contribution of a term to pressure is negative, since the molecules become ‘stickier’, the contribution of b term is positive as it is more likely for the molecules to collide. At low temperature, the effect due to a term is stronger, but as temperature increases, the effect of b term is stronger, since the molecules have more K.E at higher temperature to escape the attraction of other molecules.

6. **Solution:**

(a)

$$H = U + pV \quad (38)$$

$$dH = dU + pdV + Vdp \quad (39)$$

$$= TdS - pdV + pdV + Vdp \quad (40)$$

$$= TdS + Vdp \quad (41)$$

Under condition of constant pressure, $dp = 0$, so that $dH = TdS = Q$. Therefore, ΔH is equal to the heat flow into the system under constant pressure.

(b) As $H = U + pV$, under constant pressure, $\Delta H = \Delta U + p\Delta V$, so $\Delta U = \Delta H - p\Delta V$. First, one could convert 1 atm and 1 L into SI units, $1 \text{ atm} = 101325 \text{ Pa}$, and $1 \text{ L} = 0.001 \text{ m}^3$. Then,

$$\Delta U = 6.01 \text{ kJmol}^{-1} - (101325 * (0.018 - 0.0196) * 0.001) \text{ Jmol}^{-1} \quad (42)$$

$$= 6.0102 \text{ kJmol}^{-1} \quad (43)$$

(c) Similar to part b, $\Delta U = 37.6 \text{ kJmol}^{-1}$.

(d) As internal energy is an intrinsic property of the material, one could identify the change in internal energy (37.6 kJmol^{-1}) as the energy absorbed in overcoming the intermolecular interaction. Then, the difference between actual energy absorbed and change in internal energy $\Delta H - \Delta U = p\Delta V = 3.099 \text{ kJmol}^{-1}$ could be identified as the work done against the atmosphere.