

## Junior honours Thermodynamics Assessed Problem 4

Hand in to Teaching Office by Thursday S2 week 1: Deadline 12am Thurs 18th Jan.

1. In *molecular dynamics* calculations, it is easy to obtain  $U$  and  $H$  from averaging energies of arrangements of atoms representative of a given temperature[1]. However, even if all the atomic positions are known, there is still no way to directly calculate  $S$ ,  $F$  or  $G$ . One needs to know all possible arrangements.

Prove that

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

In a molecular dynamics calculation, the temperature is raised from  $T_1$  to  $T_2$ , at constant pressure and the heat capacity is ( $C_P = A + BT$ ). Find an expression for final Gibbs Free energy in terms of its initial value, the initial enthalpy ( $H_1$ ,  $G_1$ ) and  $C_P$ .

2. Prove the general result that

$$\left(\frac{\partial U}{\partial V}\right)_T = T^2 \left(\frac{\partial(P/T)}{\partial T}\right)_v$$

The van der Waals equation for one mole of diatomic fluid is given by

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

3. Show that the heat capacity at constant volume of a van der Waals fluid depends only on the temperature. [2]
4. Using the previous results, and the fact that in the low pressure limit the van der Waals fluid energy must be the same as the ideal gas, prove that the molar internal energy of a diatomic van der Waals fluid is given by

$$u_{vdW}(V, T) = \frac{5}{2}RT - a/v$$

and hence show that  $C_v$  is the same for the ideal gas and van der Waals fluid.

Explain the physical reason for why the constant  $a$  appears in this equation, but not the constant  $b$ .

5. Sketch the P,T phase diagram for the van der Waals fluid. Calculate the isothermal bulk modulus by differentiating the van der Waals equation in terms of  $v$  and  $T$ , give conditions for the differential to be negative, and explain what would actually happen to a van der Waals fluid under such conditions.
6. Show that the change in entropy when one mole of a van der Waals fluid converts from  $(T_0, V_0)$  to  $(T, V)$  is

$$\Delta S = \left(R \ln \frac{V - b}{V_0 - b} + C_v \ln \frac{T}{T_0}\right)$$

7. We now consider intramolecular forces. For one mole of rigid diatomic ideal gas,  $u_{bond}$  is the additional energy in the chemical bonds holding the atoms together, which can be taken as a constant. The molar internal energy is then:

$$u_{ideal}(V, T) = \frac{5}{2}RT - u_{bond}$$

Write down the internal energy for the same gas in its monatomic form. You are given that at  $T_0=3000\text{K}$ ,  $P_0 = 10^5\text{Pa}$ , the monatomic and diatomic forms of gas have the same chemical potential. Calculate the equation for the P,T phase boundary between diatomic and monoatomic gases. Sketch this phase diagram, explaining under what circumstances we might observe (i) a monatomic gas (ii) a diatomic gas (iii) a mixture of monatomic and diatomic molecules

8. A plasma is a phase of matter so hot that the electrons escape the Coulomb attraction of the nuclei and move as free particles. By considering the hydrogen atom as a diatomic molecule comprising an electron and a proton, bound by  $u_{bond} = 13.6\text{eV}$ , estimate the minimum temperature of a hydrogen plasma.

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- [1] Molecular dynamics is a method for solving Newton's equations for many particles. "Particles" need not be molecules: it can be used for anything from quarks to galaxies.
- [2] Hint: it is sufficient to show that  $\frac{dc_v}{dT} = 0$ . One method is to follow the method of Tutorial 8, q1 and use some of the tricks from Tutorial 6.