TSP-2021/22 — Thermal and Statistical Physics (Part II)

Problem sheet 1: Thermodynamics

1. **Van der Waals gas**
   Show that, for a van der Waals gas, the specific heat at constant volume, C_V, obeys
   $$\left(\frac{\partial C_V}{\partial V}\right)_T = 0.$$

2. **Potentials and thermodynamic variables**
   The Gibbs free energy of an imperfect gas containing N molecules is given, in terms of its natural variables T, p and N, by
   $$G = Nk_BT\ln\left(\frac{p}{p_0}\right) - NA(T)\,p,$$
   where p_0 is a constant and A is a function of T only. Derive expressions in terms of T, p, V, and N for:
   (a) the equation of state of the gas;
   (b) the entropy, S;
   (c) the enthalpy, H;
   (d) the internal energy, U;
   (e) the Helmholtz free energy, F.

   Can all equilibrium thermodynamic information about the gas be obtained from a knowledge of: (i) $F(T,V,N)$; (ii) the equation of state and $U(T,p,N)$?

3. **Entropy of the monatomic gas**
   The entropy of a monatomic ideal gas is given by the Sackur-Tetrode equation which can be written in the form:
   $$S(U,V,N) = Nk_B\ln\left\{\alpha\frac{V}{N}\left(\frac{U}{N}\right)^{3/2}\right\},$$
   where α is a constant to be derived later in the course.

   Invert this expression to get $U(S,V,N)$. From this, obtain the equation of state expressing p as a function of V,N and T.

4. **Analytic thermodynamics**
   Use a Maxwell relation and the chain rule to show that for any substance the rate of change of T with p in a reversible adiabatic compression is given by
   $$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{T}{C_p}\right)\left(\frac{\partial V}{\partial T}\right)_p.$$
   Find an equivalent expression for the adiabatic rate of change of T with V, and check that both results are valid for an ideal monatomic gas.

5. **Oxygen extraction**
   What is the minimum work required to extract 1 mole of pure O_2 from a large volume of air at the same temperature and pressure, if air is regarded as being composed of 1 volume of O_2 mixed with 4 volumes of N_2. [Ans. 13.4 J $K^{-1} \times T$, where T is the temperature.]

6. **Scaling**
According to Debye theory, the specific heat capacity of a crystalline solid may be expressed in the form
$$c_v = f(T/\theta)$$
where θ is independent on temperature T but depends on volume according to $\theta \propto V^{-\gamma}$, γ being a constant. Show that the isobaric expansion coefficient $\alpha = (\partial \ln V/\partial T)_p$ and the isothermal compressibility $\kappa = -(\partial \ln V/\partial p)_T$ obey the relationship
$$\alpha = \gamma c_v \kappa / V$$
[Note that the third law of thermodynamics requires that α and c_v both vanish at zero temperature]

7. **Bubble**
Under what conditions is the Helmholtz free energy F a minimum for a system in equilibrium? The work corresponding to an increase in the surface area of a liquid is $dW = \Gamma\, dA$, where Γ is the surface tension, and A is the area of the surface.

Consider a bubble of air in a large container of liquid in equilibrium. Write the total Helmholtz free energy of the system as the sum of contributions from the air in the bubble, F_a, the surface of the bubble, F_s, and the surrounding liquid, F_l. Show that the pressure of the air inside the bubble is equal to $p_l + 2\Gamma/r$, where p_l is the pressure of the liquid.

8. **Latent Heats**
At high temperature, iron has the following properties: below 900 °C and above 1400 °C α-iron is the stable modification, and between these temperatures γ-iron is stable. The specific heat capacity of each phase may be taken as constant. It is $0.775\,\mathrm{J\,g^{-1}\,K^{-1}}$ for α-iron and $0.690\,\mathrm{J\,g^{-1}\,K^{-1}}$ for γ-iron. What is the latent heat at each transition?
[Ans. $18.6\,\mathrm{J\,g^{-1}}$ and $23.9\,\mathrm{J\,g^{-1}}$]

9. **Fuel cell**
Consider the reaction
$$2\mathrm{H_2} + \mathrm{O_2} \to 2\mathrm{H_2O}.$$
The following table lists parameters for this reaction at constant temperature $T = 298$ K and pressure $p = 1$ atm.

n	H_2	O_2	H_2O (liquid)
Enthalpy $H_n^{(m)}$ (kJ/mol)	0	0	-285.8
Entropy $S_n^{(m)}$ (J/mol K)	130.7	205.1	69.9

We first consider a process, in which the reactants are mixed and the reaction proceeds towards equilibrium at constant pressure and temperature. Calculate the Gibbs free energies per mole, $G_n^{(m)}$. Calculate the equilibrium constant $K_c(p, T)$. What does its value tell us about the nature of the reaction?

We now consider an ideal fuel cell operating at the same pressure and temperature, in which the reaction proceeds via an electrolyte. What are the maximum possible electric work extracted and the corresponding heat produced when forming one mol of H_2O. What is the efficiency and the voltage of an ideal fuel cell?