

Solids and Surfaces – 3rd year Michaelmas Term

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Tutorial Problem Sheet

1. The Einstein model for the specific heat C_v of a monatomic solid predicts that this is described by the equation:

$$C_v = \frac{3R(Q_E/T)^2}{(\exp(Q_E/T) - 1)^2} \exp(Q_E/T)$$

- Explain the nature of the model, which leads to the equation above.
 - Deduce the limits of the heat capacity as $T \rightarrow 0$ and $T \rightarrow \infty$.
 - The heat capacity of diamond is $6.1 \text{ J K}^{-1} \text{ mole}^{-1}$ at 298 K. By using a method of “trial substitution” or otherwise, deduce the Einstein temperature of diamond.
 - What does Einstein’s model predict for the difference between C_p and C_v for the solid concerned?
2. The potential governing the atomic motion in Einstein’s model can be estimated from the elastic deformation of the solid under an applied force (why?), and a simple calculation indicates that the vibrational frequency ν is given by

$$\nu = \left(\frac{1}{p} \right) \left(\frac{aE}{m} \right)^{1/2}$$

where a is the bond length, E the Young’s modulus (ie applied force per unit area divided by the elastic extension produced per unit length) and m is the mass of the atom concerned. For Pb, $a = 0.32 \text{ nm}$, $E = 1.8 \times 10^{10} \text{ N m}^{-2}$ and m is 207.2 u. Calculate the Einstein temperature of Pb and the heat capacity of Pb at 298 K. Why do Pb and diamond give so different results?

3. Explain why the Einstein model fails to describe the heat capacity of simple solids at low temperatures. C_v for solid Ar has been measured for $T < 2 \text{ K}$ and the data is presented in the table below.

$C_v / \text{mJ mol}^{-1} \text{ K}^{-1}$	3.3	6.7	10	13	16.5
T / K	1.10	1.39	1.59	1.75	1.88

- (i) Show that the data is consistent with the low temperature prediction of

Debye's theory, and calculate the Debye temperature.

(ii) Calculate the entropy of solid Ar at 5 K.

(iii) Potassium has the same Debye temperature as Ar, but the heat capacity at 0.5 K is $1.4 \text{ mJ mol}^{-1} \text{ K}^{-1}$. Explain the difference between the values for K and Ar, and use the data to estimate the Fermi temperature of potassium.

4. The enthalpy of formation of a Schottky defect pair in a 1:1 ionic crystal is 10^{-19} J .

(i) Calculate the equilibrium fractional concentration, x_s , of Schottky pairs at temperatures of 300 K and 1000 K, assuming $x_s \ll 1$.

(ii) Calculate the enthalpy change, the entropy change and the Gibbs free energy change of the bulk crystal which occurs when these defects form at 1000 K.

5. Describe a model for an adsorbed layer, in which the configurational entropy is given by the expression

$$S = k \ln \left[\frac{M!}{N!(M-N)!} \right]$$

indicating how this equation is derived. M is the number of adsorption sites and N , the number of adsorbed species. This model leads to the Langmuir adsorption isotherm, but does not always give the correct predictions. Why?

6. Ammonia adsorbs on charcoal at 273 K, and the following data has been reported

P / mbar	50	100	200	400	600
x	0.056	0.084	0.111	0.134	0.143

x refers to the mass in kg of ammonia adsorbed per unit mass of charcoal. Show that the data obey the Langmuir adsorption isotherm and calculate the surface area per kg of charcoal, given that the area occupied by one ammonia molecule is $1.3 \times 10^{-19} \text{ m}^2$.

7. Nitrogen physisorbs on charcoal black at low temperatures, and the ratios of the pressures at 77 K and 90 K, required to yield a particular surface coverage, Θ , have been measured.

Θ	0.5	0.9	1.5
$p(90 \text{ K}) / p(77 \text{ K})$	9.1	10.4	4.2

Calculate the heats of adsorption at the different coverages and explain the results you obtain (latent heat of condensation of nitrogen is $5.7 \text{ J K}^{-1} \text{ mol}^{-1}$).

8. According to the “Langmuir” model, competitive adsorption of two gases A and B on the same surface, yields equilibrium surface coverages of the form

$$Q_A = \frac{K_A P_A}{(1 + K_A P_A + K_B P_B)} \quad Q_B = \frac{K_B P_B}{(1 + K_A P_A + K_B P_B)}$$

A heterogeneous catalyst catalyses the formation of CO_2 from CO and O_2 . Measurement of the kinetics shows that rate of production of CO_2 is proportional to the gas pressure of CO, inversely proportional to the gas pressure of O_2 and independent of the gas pressure of CO_2 . Suggest why this is observed.

9. What is meant by the term “surface sensitive” when applied to techniques for the study of solid surfaces? Describe the strategies which can be employed to achieve surface sensitivity.