

MOLECULAR INTERACTIONS

Attempt the following questions from recent finals papers.

NB: I've given you the complete question in each case. If parts of questions are repeated in later questions, just refer back to your previous answer - don't feel you need to write it all out again!

Q1. 1999 General Physical Chemistry I, Q9

- a) Write brief notes to explain the physical origin of the following types of intermolecular interaction:
- inductive
 - dispersive
 - repulsive

- b) The Lennard-Jones potential for the interaction of two argon atoms may be written in the form

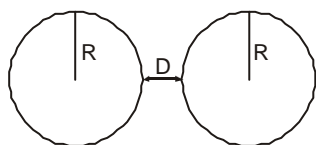
$$V(r) = 4\epsilon \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right]$$

where $r_0 = 342 \text{ pm}$ and $\epsilon = 1.712 \times 10^{-21} \text{ J}$.

- Sketch the form of this potential and state which of the types of force described above contribute to each term.
- Derive an expression for the force between the two argon atoms at an arbitrary distance r .
- Calculate the radial position of the minimum in the potential and show that the well depth is equal to ϵ .
- Assuming that in liquid argon the coordination number of each atom is 12, estimate the enthalpy of vaporization of liquid argon at 87 K. Describe any additional assumptions made in your calculation and compare your answer with the experimental value, $\Delta_{\text{vap}}H = 6.28 \text{ kJ mol}^{-1}$.

Q2. 2000 General Physical Chemistry I, Q5

- a) Van der Waals attractions occur between molecules with and without permanent dipoles. Describe qualitatively the physical origins of the three principle types of attractive Van der Waals interactions (i.e. those whose energy varies with distance as r^{-6} .)
- b) Attractive van der Waals interactions between individual molecules are usually weak ($\leq kT$ at room temperature) and short range; interactions between colloidal particles are generally strong ($\gg kT$) and long range. Comment on the consequences for the stability of colloids.
- c) Two polystyrene spheres with polarisability α per unit volume and radius R are separated by a distance D .



The attractive part of the pair potential for the two particles has the form

$$U = -\frac{AR}{12D} \quad \text{for } D \ll R$$

where the Hamaker constant $A = 1.0 \times 10^{-19} \text{ J}$ for polystyrene spheres in a vacuum.

Estimate the interaction energy between the two particles of radius $0.5 \mu\text{m}$ and separation $0.1 \mu\text{m}$. Compare the interaction energy to the thermal energy at 298 K .

Would the interaction between the two spheres be weaker or stronger in water than in a vacuum?

d) The two spheres are placed in a uniform electric field of strength E . Explain how this field gives rise to an additional interaction between the two spheres, which can be either positive or negative depending on the direction of the electric field.

Show that the repulsive interaction energy due to the field has a maximum value of

$$U = \frac{[(4/3)\pi R^3]^2 \alpha^2 E^2}{4\pi\epsilon_0(D+2R)^3}$$

Note: the interaction energy between two parallel point dipoles separated by a distance r in a vacuum is

$$U = \frac{\mu^2}{4\pi\epsilon_0 r^3}$$

Q3. 2000 General Physical Chemistry II, Q9

a) The Random Flight Model is the simplest model for describing the conformations of polymer chains in solution. A polymer is treated as consisting of N segments, each of which is characterised by a vector \mathbf{l}_k of length l . In the Random Flight Model, the orientations of these segments are random, i.e. $\langle \mathbf{l}_j \cdot \mathbf{l}_k \rangle = 0$, where j and k are two *different* segments. The vector \mathbf{R} connecting the two ends of the polymer is

$$\mathbf{R} = \sum_{k=1}^N \mathbf{l}_k$$

Show that the mean square distance between the two ends can be written

$$\langle R^2 \rangle = \langle \mathbf{R} \cdot \mathbf{R} \rangle = N l^2$$

Calculate the predicted value, in the Random Flight Model, of the root-mean-square end-to-end distance, $\langle R^2 \rangle^{1/2}$, for polyethylene oxide of molecular weight 10^6 u , taking the segment to be $(\text{CH}_2\text{CH}_2\text{O})$ with a molecular weight of 44 u and a length of 0.36 nm .

The value of $\langle R^2 \rangle^{1/2}$ inferred from light scattering is 110 nm . Comment on the Random Flight Model in the light of this value.

b) Man-made polymers have several features that distinguish their behaviour from that of small molecules, for example, a high molecular weight, polydispersity, and a large contribution to the standard entropy from different chain conformations. Explain how these factors play a role in THREE of the following observations on the behaviour of polymers.

- i) For most polymers, determination of the molecular weight by osmotic pressure measurements and by light scattering give different values;
- ii) Polymer solutions show large deviations from ideality;
- iii) Rubber warms up if it is stretched adiabatically (for a metal spring, only a very small temperature change is observed);
- iv) Weakly adsorbed polymers stabilize colloids against coagulation;
- v) The radius of gyration of polystyrene in cyclohexane increases with increasing temperature.

Q4. 2001 General Physical Chemistry I, Q9

a) Explain what is meant by the *second virial coefficient* of a gas.

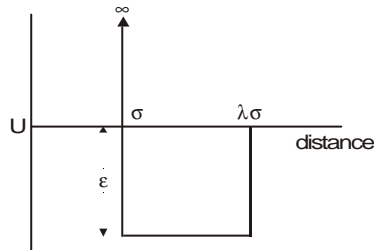
b) The second virial coefficient B of a gas is related to the intermolecular potential U between two molecules at a distance r by

$$B = 2\pi \int_0^{\infty} (1 - e^{-U/kT}) r^2 dr$$

i) Show that for molecules that behave like hard spheres of diameter σ ($U = \infty$ when $r < \sigma$, $U = 0$ when $r > \sigma$) the virial coefficient is given by

$$B = \frac{2\pi \sigma^3}{3}$$

ii) For real molecules there is also an attractive interaction. An approximate representation of the interaction potential can be made using the square well potential shown below.



Show that the expression for the virial coefficient now becomes

$$B = \frac{2\pi \sigma^3}{3} [\lambda^3 + (1 - \lambda^3)e^{\epsilon/kT}]$$

iii) The temperature at which N_2 behaves like an ideal gas (the Boyle temperature) is 325 K. Given that λ is 1.58 for N_2 use the value of the Boyle temperature to calculate the depth ϵ of the square well potential.

iv) Experimentally determined values of the second virial coefficient of N_2 at lower temperatures are given below.

T / K	100	125	175	250
$B / \text{cm}^3 \text{ mol}^{-1}$	-163.6	-104.8	-50.1	-16.2

Using the values of ϵ and λ from iii) show that the square well potential accounts accurately for the data in the table above. Use the data to calculate σ .

v) What other experimental information could be used to show that the square well potential is not an accurate representation of the true intermolecular potential?

Q5. 2001 General Physical Chemistry II, Q7.

a) Sketch a diagram of the typical behaviour of the surface tension of an aqueous solution of a surfactant over a concentration range from well below the critical micelle concentration to just above it.

b) The adsorption of a non-ionic surface active agent at the air surface of an aqueous solution obeys the Gibbs equation

$$d\gamma = -\Gamma RT d \ln c$$

The values of the surface tension for an aqueous solution of a soluble polymeric surfactant at concentrations just below its critical micelle concentration (10^{-3} M) at 300 K are given below.

concentration / M	5×10^{-5}	1×10^{-4}	5×10^{-4}	1×10^{-3}
surface tension / 10^{-3} Nm ⁻¹	37.4	36.5	34.4	33.9

Use these data to calculate the surface excess of the surfactant and hence calculate the area per molecule at the air/water interface.

c) The hydrophilic part of the polymeric surfactant in part b) consists of a number of ethylene oxide (EO) segments. The area per molecule occupied by the small molecule surfactant $C_{12}H_{25}(OC_2H_4)_6OH$ just below its critical micelle concentration is 0.55×10^{-18} m².

Assuming that the area per EO segment is the same for the two surfactants in their saturated monolayers, estimate the number of EO groups in the polymeric surfactant.