Physical Basis of Chemistry

Electricity and magnetism

Problems labelled A are straightforward, those marked B are supposed to be more demanding, those marked C are intended to make you think.

1 Coulomb's law

1.1A In the Bohr model of the hydrogen atom an electron circulates the nucleus in a circular orbit of radius 52.9 pm. Calculate the electrostatic force on the electron in such an orbit.

1.2A Calculate the electrostatic force between a Na+ ion and a Cl – ion separated by 11.3 Å (i) in vacuum; (ii) in aqueous solution (ε_r = 78).

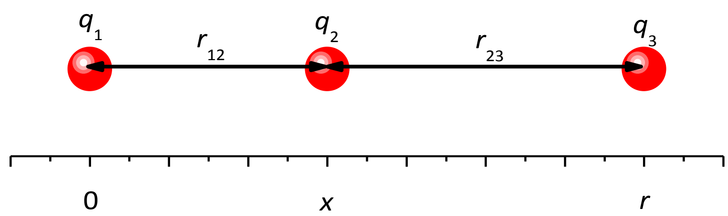
1.3A A HeH^+ ion is slammed into a surface and loses both its electrons in the collision. The HeH^+ bond length is 79 pm. Calculate the repulsive force between the two nuclei. This is called a Coulomb explosion. [*Chem. Rev.* 1980, **80**, 301]

1.4A Cubic [Fe_4S_4] complexes are very common electron transfer centres in biological systems. In a mass spectrometer the $[Fe_4S_4Cl_4]^{2-}$ complex spontaneously breaks apart into two equal fragments. The initial repulsive force between the fragments is 445 pN. Calculate the distance between the fragments at this point. [*Phys. Rev. Lett.* 2002, **89**, 163401]

1.5B A charge $+e$ is located at $(-d/2,0,0)$ and a charge $-e$ is located at $(+d/2,0,0)$. Find the force on a charge q at the points (i) $(a,0,0)$, (ii) $(-a,0,0)$, (iii) $(0,0,0)$, (iv) $(0,+a,0)$, (v) $(0,-a,0)$, (vi) (a,a,a).

1.6B A charge q is divided into two parts. What division will maximize the repulsive force?

1.7B Three positively charged particles lie on a straight line. Their charges are q_1, q_2 and q_3, with positions 0, x and r, respectively, so that the distances $r_{12} = x$ and $r_{23} = r - x$.



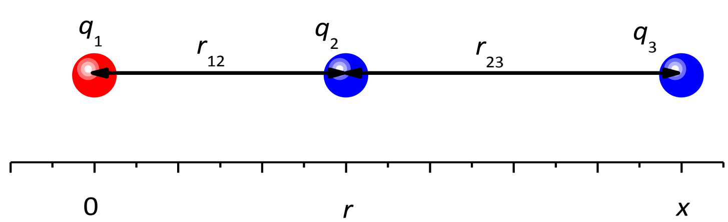
Charges 1 and 3 are fixed, charge 2 is movable.

(a) Show that at the equilibrium point for particle, 2 $q_1 r_{23}^2 = q_3 r_{12}^2$.

(b) Hence show that at equilibrium $x = r/\sqrt{1 + q_3/q_1}$.

(c) Show that at equilibrium the electrostatic forces on particles 1 and 3 are equal and opposite. Comment on this result.

1.8B Three charged particles lie on a straight line. Their charges are q_1, q_2 and q_3, with positions 0, r and x, respectively, so that the distances $r_{12} = r$ and $r_{23} = x - r$.



Particle 1 is positively charged and particles 2 and 3 are negatively charged. Particles 1 and 2 are fixed, particle 3 is movable.

(a) Show that at the equilibrium point for particle 3, $q_1 r_{23}^2 = -q_2 r_{13}^2$.

(b) Hence show that at equilibrium, $x = r\dfrac{1+\sqrt{|q_2|/q_1}}{1-|q_2|/q_1}$. Explain the difference between the cases $|q_2| < q_1$ and $|q_2| > q_1$. Why is there no solution when $|q_2| = q_1$?

1.9B Suppose that the three charges in problem 1.7 are equal, and the central particle is displaced slightly along the axis from its equilibrium position. Find an expression for the restoring force on the displaced particle, and show that for a small displacement δx the restoring force is to first order $-32q^2\delta x / 4\pi\varepsilon_o r^3$ (such a particle would undergo simple harmonic motion).

2 Electric field

2.1A Calculate the electric fields in problems 1.1 to 1.5.

2.2B Show that the electric field at the origin from the following charge configurations is exactly zero: (these are the partial charges on atoms in the following molecules)
(i) Charges of $-0.31e$ along the x axis at ±1.162 Å (O atoms in CO_2).
(II) Charges of $-0.15e$ equidistant from the origin at a distance of 1.307 Å arranged in an equilateral triangle in the xy plane (F atoms in BF_3).

2.3B Given the following coordinates and partial charges (for H_2O) find the electric field at the point (0,0,10) Å.

Atom	***x* / Å**	***y* / Å**	***z* / Å**	***q*/*e***
O	0.0000	0.0000	0.1173	–0.6568
H	0.0000	0.7572	-0.4692	+0.3824
H	0.0000	-0.7572	-0.4692	+0.3824

2.4B Given the following coordinates and partial charges (for NH_3) find the electric field at the point (0,0,10) Å.

Atom	***x* / Å**	***y* / Å**	***z* / Å**	***q*/*e***
N	0.0000	0.0000	0.0000	–0.8022
H	0.0000	-0.9377	-0.3816	+0.2674
H	0.8121	0.4689	-0.3816	+0.2674
H	-0.8121	0.4689	-0.3816	+0.2674

2.5A Sketch the electric field lines for a system of two equal and opposite charges.

2.6B In systems such those of problems 1.7 and 1.8, explain why the equilibrium position of the movable charge does not depend on the value of its charge.

2.7C A cable consists of a wire of radius r_1 embedded coaxially in a dielectric cylinder with dielectric constant ε_r and surrounded by a metal braid of radius r_2. If the charge per unit length on the wire is λ, and that on the braid is $-\lambda$, find an expression for the electric field (i) between the wire and the braid; (ii) outside the braid. Use Gauss's law.

2.8C In a hydrogen atom there is a nucleus of charge +e at the origin, surrounded by an electron density $\rho = \dfrac{\exp(-2r/a_o)}{\pi a_o^3}$.

(i) Verify that this density is normalized, i.e. that $\int_0^\infty 4\pi r^2 \rho\, dr = 1$.

(ii) Use Gauss's law to find the enclosed charge within a sphere of radius *r*, and hence the electric field in the hydrogen atom as a function of distance from the nucleus. You may use the result $\int r^2 \exp(-\alpha r)\, dr = -\alpha^{-3}\ \ 2+2\alpha r+\alpha^2 r^2\ \ \exp(-\alpha r)$.

(iii) Defining an effective nuclear charge *Z*(*r*) such that $E(r) = \dfrac{Z(r)e}{4\pi\varepsilon_o r^2}$, find an expression for *Z*(*r*) and sketch it.

3 Potential energy and potential

3.1A [Prelim June 2009] (a) Write an equation for the potential energy of interaction of two ions of charge z_1 and z_2 in a medium of relative permittivity (dielectric constant) ε_r.
(b) Calculate the distance at which the coulomb interaction between ions of unit charge is equal to kT: (i) in water $\varepsilon_r = 78$; (ii) in hexane $\varepsilon_r = 1.89$. Comment on the likelihood of a reaction between similarly charged ions in each solvent.

3.2A [Prelim June 2009]The ionisation energy of the K atom is 419 kJ mol^{-1} and the electron affinity of the Br_2 molecule is 245 kJ mol^{-1}
(a) Calculate the energy required to convert a K atom and a Br_2 molecule to the ionised species K^+ and Br_2^- at infinite separation.
(b) Calculate the separation at which the energy of attraction of the ionised species in vacuo is equal to the energy required to form them from the neutral species.

3.3A Calculate the potential energy of electrostatic interaction between a sodium ion and a chloride ion separated by 1.5 nm (i) in a vacuum, (ii) in aqueous solution (dielectric constant 80.4).

3.4A In a sodium chloride crystal each ion is surrounded by six nearest neighbours at a distance of 0.276 nm. Estimate the contribution to the potential energy of a sodium ion from interaction with the six nearest neighbours.

3.5B A TV tube contains two parallel plates 7.5 mm apart. If a pd of 150 V is maintained between them
(i) calculate the electric field strength in the gap.
(ii) calculate the force on an electron in the gap.
(iii) an electron is emitted from the negative electrode with negligible velocity, calculate the time it takes to cross the gap.

3.6A The electron volt (eV) is a unit which is frequently used to measure energies on an atomic scale. One electron volt is the kinetic energy gained by an electron when it is accelerated through a potential difference of 1 V. Calculate the conversion factor from eV to J.

3.7B In the acceleration phase of a mass spectrometer positive ions are accelerated through a potential difference of 10.0 kV. Calculate the kinetic energy and the speed of (i) CH_4^+ and (ii) $C_6H_6^+$ ions after acceleration through this field.

3.8B Two square metal plates of side 50 cm are fixed 2.0 cm apart and are maintained at a potential difference of 1.0 kV. The gap is filled with liquid cyclohexane, whose dielectric constant is 1.9.

(i) Calculate the electric field strength in the gap.

(ii) Calculate the force on a molecular singly charged cation between the plates.

(iii) Calculate the capacitance of the system and the stored charge.

3.9C Find an expression for the electric potential in the region between the wire and the braid in problem 2.7. Hence deduce the potential difference between the wire and the braid and the capacitance per unit length.

4 Millikan experiment

4.1A Calculate the radius of a water drop that would remain just suspended in the earth's electric field, 120 V m^{-1}. Calculate also the surface charge density at the earth's surface.

4.2A Calculate the pd necessary to be maintained between two parallel plates 5.0 mm apart in order to suspend in equilibrium a small oil drop of mass 1.31×10^{-14} kg with an electronic charge of $-2e$.

4.3B A uniform electric field 500 kV m^{-1} acts vertically downwards. A small oil drop carrying charge 8e falls with a uniform speed of 200 μm s^{-1}. If the charge is increased to 11e, it moves upwards with a speed of 100 μm s^{-1}. Find

(i) the mass of the drop;

(ii) the charge it would carry if it were suspended at equilibrium in the field.

4.4C In Millikan's experiment two consecutive measurements were as follows with a drop distance of 10.21 mm. The drop (drop 14) was timed at 18.804 s in its fall, and then when a potential difference of 5075 V between the plates separated by 16 mm, it rose through the same distance in 65.416 s. In the next measurement with the same drop the fall time was 18.662 s and the rise time 118.97 s. Calculate the charge on the drop in the two experiments and the difference between these charges. You may use the following data: T = 296.25 K, p = 100.4 kPa, $\eta = 1.825\times10^{-5}$ kg m^{-1} s^{-1}, g = 9.80 m s^{-2}, ρ_{oil} = 919.9 kg m^{-3}, ρ_{air} = 1.2 kg m^{-3}, $b = 7.88\times10^{-3}$ Pa m.

5 Dipole moments

5.1A The Cl atom in the ClF_3 molecule is surrounded by 5 electron pairs arranged in a trigonal bipyramid. 3 of these are bonding pairs and the remaining 2 are lone pairs. If the molecule has a non-zero dipole moment, what is its structure?

5.2B [Prelim Sept 2003] The CsCl molecule has an equilibrium internuclear distance of 360 pm. Assuming that there is complete charge transfer, calculate:
(i) its electric dipole moment in debye (D);
(ii) the coulombic contribution to the bond energy.

5.3B [Prelim June 2008] (a)Define the dipole moment of a neutral molecule.
(b) The dipole moment of SO_2, a bent molecule, is 1.60 D, the bond angle is 120° and the S – O bond length is 143 pm. Determine the partial charge on each of the atoms.

5.4A The dipole moment of a C=O bond is 2.70 D and the bond length is 0.122 nm. Calculate the effective charges on the two atoms and hence estimate the percentage ionic character of the bond.

5.5A A water molecule (dipole moment 1.80 D) approaches an anion. What is the most favourable orientation of the water molecule with respect to the anion? Calculate the potential energy of the interaction at a distance of 1.0 nm and compare this to thermal energy ($3kT/2$). [Don't forget the dielectric constant of water is 80.4].

5.6B Find the dipole moments of the molecules in problems 2.3 and 2.4. Assuming this to be a point dipole at the origin, calculate the electric field at the point (0,0,10) Å. Compare this with the values you obtained earlier.

5.7B Find an expression for the energy of a dipole in a uniform electric field parallel to the z axis as a function of the angle between the dipole and the field.

5.8B A diatomic dipole with partial charges $\pm q$ and a separation d is oriented at an angle θ relative to a constant electric field $\mathbf{E}$. Find the resulting force on each atom and resolve it into components parallel to the dipole (stretching) and perpendicular to the dipole (turning).