University of Reading

FIRST YEAR UNDERGRADUATE CHEMISTRY

PHYSICAL CHEMISTRY WORKBOOK

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'SKILLS FOR SCIENTISTS'

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Physical Chemistry Workbook

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The workbook contains a selection of typical questions with worked answers on the topics above. Following the example questions are questions which students can attempt themselves of a similar type. Worked answers can be found to the questions at the end of each section.

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Basic Chemical Calculations

Worked example 1 Numbers of Moles and Numbers of Atoms

a) Why, in chemistry, do we use the concept of *moles*, and what is it *one mole* defined as?

b) How many moles are in the following. Use the data box below.

i) 1 g of solid carbon

ii) 10 g of selenium

iii) 1 g of chlorine gas (Cl_2)

c) For i) – iii) deduce how many atoms are present.

DATA:

Element	**Molar Mass/ g mol^{-1}**
carbon	12.0
chlorine	35.45
selenium	79.0

Answers to Worked Example 1

a) Moles are a system used to describe the amount of species, in a standardised, universal manner. It is of use in many chemical applications as it is standardised with respect to carbon-12. One mole is defined as the number of carbon atoms present in exactly 12 g of carbon-12.

b)i) Using:

Number of moles = Mass (g) / M (g mol^{-1})
= 1 g / 12.0 g mol^{-1}
= 0.0833 mol

ii) Similarly,

Number of moles = 10 g / 79.0 g mol^{-1}
= 0.127 mol

iii) Number of moles = 1 g / 35.5 g mol^{-1}
= 0.0282 mol of chlorine atoms
So moles of chlorine molecules is half this amount
Number of moles (Cl_2) = 0.0282 mol / 2
= 0.0141 mol

c)i) Using:

Number of atoms = Number of moles x Avogadro's number
= 0.0833 mol x 6.022 x 10^{23} atoms mol^{-1}
= 5.02 x 10^{22} atoms

ii) As above,

Number of atoms = Number of moles x Avogadro's number
= 0.127 mol x 6.022 x 10^{23} atoms mol^{-1}
= 7.65 x 10^{22} atoms

iii) *Number of atoms = Number of moles x Avogadro's number*
= 2 x 0.0141 mol x 6.022×10^{23} *atoms* mol^{-1}
= 1.70×10^{22} *atoms*

Question 1

a) What is the mass of 0.5 mol of solid silver? (M = 108 g mol^{-1})

b) How many moles are there in 11.05 g of propanoyl chloride, CH_3CH_2COOCl?

DATA

Element	Molar Mass / g mol^{-1}
Hydrogen	1.01
Carbon	12.01
Oxygen	16.00
Chlorine	35.5
Silver	108.0

Worked Example 2 Calculating Masses from Moles and Moles from Masses

a) Define the term *Molar Mass* (M) and give the formula for its calculation in terms of the number of moles present in a sample and the mass of the sample.

b) A student performs an experiment to produce the ester methyl ethanoate, CH_3COOCH_3, from methanol, CH_3OH, and ethanoic acid, CH_3COOH.
   i) What are the Molar Masses of the reactants?
   ii) Given that she starts with 0.5 moles of both reactants, what is the total mass of the reagents at the start of the reaction?
   iii) Her purified product weighs 8.0 g. How many moles of ester has she produced?

Answers

a) *The molar mass is the mass per mole of a species. It is given by:*
Molar Mass = Mass of sample / Number of moles in sample

b) *To answer this we must sum the molar masses of each element multiplied by how many atoms of that element are present in each molecule:*

M (methanol) = 12.0 g mol^{-1} *x 1 mol + 1.0 x 4 + 16.0 x 1 = 32.0 g* mol^{-1}

M (ethanoic acid) = 12.0 g mol^{-1} *x 2 mol + 1.0 x 4 + 16.0 x 2 = 60.0 g* mol^{-1}

c) Using:
Mass = M x number of moles
i) Mass (methanol) = 32.0 g mol^{-1} *x 0.5 mol = 16.0 g*
ii) Mass (ethanoic acid) = 60.0 g mol^{-1} *x 0.5 mol = 30.0 g*

So total mass of reagents = 16.0 g + 30.0 g = 46.0 g

d) To calculate how many moles of ester are produced we will need to know the M of the ester:
M (methyl ethanoate) = 12.0 g mol^{-1} *x 3 mol + 1.0 g* mol^{-1} *x 6 mol+ 16.0 g* mol^{-1} *x 2 mol = 74.0 g* mol^{-1}
Then we rearrange the equation used in c) to make "number of moles" the subject:
Number of moles = Mass (g) / M (g mol^{-1}*)*
= 8.0 g / 74.0 g mol^{-1}
= 0.11 mol of product

Question 2

a) By use of a periodic table, determine the molar masses (M) of:
i) Fluorine, F_2

ii) Carbon dioxide, CO_2

iii) Dichloroethene, $C_2Cl_2H_2$

b) Hence what is the mass (in g) of:
i) 1 mole of fluorine gas

ii) 2.54 moles of carbon dioxide

iii) 0.23 moles of dichloroethene

Worked Example 3 **Empirical and Molecular Formuale**

A green compound is known to contain only chromium and oxygen. It is found to contain 68.42% chromium.
a) What is the empirical formula of the compound?

b) A mass spectrometer shows the molecular mass to be 152 g mol^{-1}
What is its molecular formula?

Answers

a) If it contains 68.42% chromium, it must contain (100-68.42) = 31.58% oxygen, as the question says it contains only Cr and O.
If we consider 100 g of the compound we see that it contains 68.42 g Cr, and 31.58 g O. Converting these to moles we have:

Number of moles = Mass (g) / M (g mol^{-1}*)*
= 68.42 g / 52.0 g mol^{-1}
= 1.316 mol of Cr

and

Number of moles = Mass (g) / RAM (g mol^{-1}*)*
= 31.58 g / 16.0 g mol^{-1}
= 1.974 mol of O

The ratio of the two elements is therefore:

Cr : O
1.316 : 1.974 (divide through by the lowest number, i.e. 1.316)
1 : 1.5 (multiply out to produce integer values)
2 : 3

so the empirical formula is Cr_2O_3
b) First we must find the molecular mass of our empirical formula unit:
M of unit = (52.0 x 2) + (16.0 x 3) = 152.0 g mol^{-1}
So the mass of the empirical formula equals the molecular mass, thus Cr_2O_3 *must be our molecular formula.*

Question 3

Styrene is formed of only hydrogen and carbon, and is found to be 92.3% carbon by mass. What is the empirical formula of styrene?

Question 4

Adrenaline is found to be 59.1% carbon, 7.0% hydrogen, 26.2% oxygen and 7.7% nitrogen by mass. It has a molecular mass of around 180 g mol^{-1}.

a) What is its empirical formula?

b) What is its molecular formula?

Worked Example 4 Calculating Concentrations in Solution - Molarity

a) Define the term *Molarity.*

b) 25.0 g of NaCl was dissolved in 2 dm^3 of water. What is the molarity of the resultant solution?

c) What mass of pure $CuSO_4$ solid must be dissolved in a 50 cm^3 portion of water to ensure a final concentration of 2.521 mol dm^{-3}?

DATA

Element	**Molar Mass / g mol^{-1}**
Oxygen	16.00
Sodium	23.00
Sulfur	32.0
Chlorine	35.5
Copper	63.5

Answers

a) The molarity is defined as the number of moles of a substance per dm^3 of solution. It is given by the equation:

Molarity = Number of moles of solute (mol) / Volume of Solution (dm^3)

b) To complete the above equation we must first find how many moles of NaCl are in 25.0 g. We use the formula:

Number of moles = Mass (g) / M (g mol^{-1})
= 25.0 g / (23+35.5) g mol^{-1}
= 0.427 mol

We are told there is 2 dm^3 of solution, so the Molarity is given by:

Molarity = Number of moles of solute (mol) / Volume of Solution (dm^3)
= 0.427 mol / 2 dm^3
= 0.214 mol dm^{-3}

c) We must first find how many moles would be required to give this concentration, in this volume of liquid. We are told the volume is 50 cm^3, but for our equation we require it in units of dm^3. This is achieved by knowing that there are 1000 cm^3 in 1dm^3, thus 50 cm^3 is 0.05 dm^3.
Rearranging the above equation yields:
Number of moles = Molarity (mol dm^{-3}) x Volume of solution (dm^3)
= 2.521 x 0.05
= 0.126 mol
Given the M of $CuSO_4$, calculated by summation of the M's of the constituent atoms, we can deduce the mass of $CuSO_4$ in 0.126 moles.
M ($CuSO_4$) = 63.5 + 32 + (16 x 4) = 159.5 g mol^{-1}
So using the equation:
Mass = Number of moles x M
= 0.126 g x 159.5 g mol^{-1}
= 20.1 g

Question 5

a) What is the molarity of the solution formed when 20.3 g of sodium sulphate, $NaSO_4$, is dissolved in 250 mL of water?

b) Calculate the molarity of a solution that contains 0.0345 mol NH_4Cl in 400 mL of water.

c) Calculate the molarity of a solution made from 0.0930 mol of NaCl made up to 500 mL of solution.

d) Give the concentrations of both ions in a 0.56 mol dm^{-3} solution of NaOH.

e) What are the concentrations of Ca^{2+} and Br^- in a 0.30 M solution of $CaBr_2$?

Question 6

a) How many moles of $KMnO_4$are present in 75.5 mL of a 5.4 mol dm^{-3} solution of potassium permanganate?

b) How many moles of HNO_3 are present in a 25.0 cm^3 aliquot of a 0.0650 M solution of nitric acid?

c) Which contains the greater number of moles of Cl^-: 30.0 mL of 0.37 mol dm^{-3} KCl or 40.5 mL of 0.30 M $CaCl_2$?

Question 7

a) How many grams of solute are there in 0.250 dm^3 of a 0.100 mol dm^{-3} solution of KBr.

b) What mass of solute is present in 20 mL of a 1.87 mol dm^{-3} solution of $KClO_3$?

Worked Example 5 Converting Concentration Units

a) Convert 0.50 mol dm^{-3} to mol cm^{-3}

b) Convert 0.01 mol dm^{-3} to μmol dm^{-3}

c) Express 1 dm^3 in m^3

d) What is the molarity of a 0.25 M solution expressed in mmol cm^{-3}

Answers

a) "0.50 mol dm^{-3}" means that there are 0.50 mol in a dm^3. There are 1000 cm^3 in 1 dm^3 thus we have 1/1000 the amount of substance in 1cm^3 than in 1dm^3. This means that we have 0.50/1000 moles in one cm^3, which is 0.5 x 10^{-3}mol cm^{-3}. (Think! Are there more or less moles in a dm^3 than a m^3)

b) The suffix "μ" means "x10^{-6}" thus a mole is 10^6 times greater than a μmol, thus 0.01 mol dm^{-3} is 0.01 x 10^6 μmol dm^{-3} = 1.0 x 10^4 μmol dm^{-3}.

c) 1 dm = 10 cm = 0.1 m
hence 1 $dm^3 = 10^3 cm^3 = 0.1^3 m^3 = 10^{-3} m^3$

d) We know 1M = 1 mol dm^{-3}
We convert mol dm^{-3} to mmol dm^{-3} as we did in b) but, in this case, the former is 10^3 greater than the latter hence:
0.25 M = 0.25 mol dm^{-3} = 0.25 x 10^3 mmol dm^{-3}
We now convert dm^3 to cm^3 as follows:
1 dm = 10 cm
thus 1 $dm^3 = 10^3 cm^3 = 1000 cm^3$
Putting these two together gives us:
0.25 M = 0.25 x 10^3 mmol dm^{-3} = 0.25 x 10^3 mmol $(10cm)^{-3}$
= 0.25 x 10^3 x 10^{-3} mmol cm^{-3}
= 0.25 mmol cm^{-3}

Question 8

a) Convert 0.02 mol dm^{-3} in mol cm^{-3}

b) Convert 5 mol cm^{-3} to mol dm^{-3}

c) Convert 0.15 mol dm^{-3} to mmol dm^{-3}

d) Convert 0.10 mol dm^{-3} to μmol cm^{-3}

e) Express 500 cm^3 in dm^3

f) Express 20 cm^3 in m^3

g) Express 0.1 m^3 in dm^3

h) Express 2 dm^3 in cm^3

i) Express 1 m^2 in cm^2

j) Express 5 m^{-3} in dm^{-3}

k) Express 0.1 m^{-3} in cm^{-3}

l) Express 10 cm^{-3} in dm^{-3}

Basic Chemical Calculations Answers

1a) 54 g

b) 0.102 mol

2a)

i) 38.0

ii) 44.0

iii) 97.0

b)

i) 38.0 g

ii) 111.76 g

iii) 22.31 g

3) CH

4a) $C_9H_{13}O_3N$

b) $C_9H_{13}O_3N$

5a) 0.682 mol dm^{-3}

b) 0.0863 mol dm^{-3}

c) 0.186 mol dm^{-3}

d) When dissolved in solution, NaOH obeys the following equation:

$NaOH \rightarrow Na^+ (aq) + OH^- (aq)$

Looking at the stoichiometry of the above equation we see that 1 mol of NaOH dissolves to form 1 mol of Na^+ and 1 mol of OH^- in solution. To form a 0.56 mol dm^{-3} solution, we dissolved 0.56 mol NaOH in 1 dm^3 of solution. This must, therefore have formed 0.56 mol of Na^+ and 0.56 mol of OH^- in the dm^3 of solution. Hence, our final concentrations:

Na^+ = 0.56 mol dm^{-3}

OH^- = 0.56 mol dm^{-3}

e) When dissolved in solution, $CaBr_2$ obeys the following equation:

$CaBr_2 \rightarrow Ca^{2+} (aq) + 2Br^- (aq)$

If we look at the stoichiometry of the above equation we can see that 1 mol of $CaBr_2$ produces 1 mol of Ca^{2+} and 2 mol of Br^- in solution. In our 0.30 mol dm^{-3} solution therefore, there must be 0.3 mol dm^{-3} of Ca^{2+} and (2 x 0.3 mol dm^{-3}) of Br^- (because, according to the equation, we produce twice as much Br^- as we dissolve $CaBr_2$.)

Hence our final concentrations:

Ca^{2+} = 0.30 mol dm^{-3}

Br^- = 0.60 mol dm^{-3}

6a) 0.408 mol

b) 1.63×10^{-3} mol

c) There is 0.0111 mol in the KCl solution, and 0.0122 mol in the $CaCl_2$ solution, hence there are more moles of Cl^- in the $CaCl_2$ solution.

7a) 2.98 g

b) 4.58 g

8a) 0.02×10^{-3} mol cm^{-3}

b) 5×10^3 mol dm^{-3}

c) 0.15×10^3 mmol dm^{-3}

d) 10^2 μmol cm^{-3}

e) 500×10^{-3} dm^3 = 0.5 dm^3

f) 20×10^{-6} m^3 = $2 \times 10^{-5} m^3$

g) 0.1×10^3 dm^3 = 100 dm^3

h) 2×10^3 cm^3

i) 10^4 cm^2

j) 5×10^{-3} dm^{-3}

k) 0.1×10^{-6} cm^{-3} = 10^{-7} = cm^{-3}

l) 10×10^3 dm^{-3} = 10^4 dm^{-3}

Thermodynamics 1

1) Define:
   a) An open system

   b) A closed system

   c) An isolated system

2) Define the following as *open, closed* or *isolated:*
   a) A tightly stoppered bottle of lemonade

   b) The earth

   c) A polystyrene beaker of tea with a lid

   d) A torch battery

3) If work is defined as:
   Work done = Force x Distance
   and force is measured in Newtons,
   a) Obtain the units of 'work done'

   b) What are the derived units of force?

   c) Hence, what are the derived units of work?

   d) What is the SI symbol and unit given to this derived unit?

4) The First Law of Thermodynamics can be expressed as:

$\Delta U = q + w$

Define the terms in the above expression, and give their units

5)

a) Explain the meaning of the following terms and state the appropriate expression of the First Law of Thermodynamics:

i) An adiabatic system

ii) A non-adiabatic system

b) Explain the meaning of the following terms

i) isothermal

ii) reversible expansion

6)

a) A reaction is carried out in which 1.23 kJ of heat is released and the reaction system does 235 J work on the surroundings. What is ΔU for the process?

b) During a reaction 2.87 kJ of heat is absorbed and the reaction system does 445 J of work on the surroundings. What is ΔU for the reaction?

c) When a reaction is run at constant volume 8.69 kJ of heat was absorbed: when run at constant pressure, 8.15 kJ is absorbed. What is ΔU for the reaction?

d) A reaction run at constant volume releases 46.9 kJ. When the same reaction is run at constant pressure it releases 45.8 kJ. What is the work done on the system when it is run at constant pressure?

7)

a) What is meant by a state function?

b) What is the opposite of a state function?

c) Define the following as state or path functions:

i) Work

ii) Density

iii) Internal Energy

iv) Heat

8)

a) Explain the difference between an intensive and an extensive property.

b) Define the following properties as intensive or extensive:

i) Density

ii) Colour

iii) Volume

iv) Temperature

v) Electrical resistance

vi) Pressure

9)

a) Give an expression for the work done by a gas in a piston as it expands by a volume ΔV against an external pressure P_{ex}.

b) Hence give an expression for the change of internal energy of a system as it expands by ΔV against an external pressure, P_{ex} on absorbing q Joules of heat.

10) A gas expands from a volume of 2.50 dm^3 to 3.70 dm^3 against an external pressure of 1.50 bar while absorbing 78.0 J of heat. What is the change in internal energy of the gas in Joules, given that 1dm^3 bar = 99.98 J?

Thermodynamics 1 Answers

1i) An open system has the ability to exchange energy *and* matter with the surroundings, like an open conical flask.
ii) A closed system can exchange energy *but not* matter with the surroundings, e.g. an ice-pack for treating sports injuries.
iii) An isolated system cannot change anything with its surroundings, i.e. no energy or matter enters or leaves the system. This can be approximated (but not rigorously modelled by) a thermos flask, where a vacuum insulates the contents from heat loss to the surroundings.

2a) Closed
b) Open
c) (Approximately) Isolated, although strictly speaking some heat would be lost so it could be modelled as a closed system
d) Closed

3a) Newton metres (Nm)
b) Force = Mass x Acceleration, units = kg m s^{-2}
c) Work Done = Force x Distance = kg m s^{-2} m = kg m^2 s^{-2}
d) Joules (J)

4 ΔU = *Change in* internal energy of the system (J)
q = Energy transferred to system as heat (due to a temperature difference between system and surroundings) (J)
w = Energy transferred to system by doing work on it (J)

5 a) i) A closed system with no transfer of heat energy between the system and the surroundings.
Expression: $\Delta U = w$, so $q = 0$.
ii) A closed system in which heat may be transferred freely between system and surroundings.
Expression: $\Delta U = q + w$
Note if no work is done on or by the system…
Expression: $\Delta U = q$
b) i) a change that occurs at constant temperature

ii) expansion that takes place against an external pressure matched to the pressure of the system

6i) $\Delta U = q + w = -1230 - 235 = -1465$ J = -1.465 kJ (both heat lost to and work done on the surroundings by the system)

ii) $\Delta U = q + w = +2870 - 445 = +2425$ = +2.425 kJ (heat absorbed by system so positive, but work done on surroundings by system so negative)

iii) At constant volume, no work is done thus ΔU = 8.69 kJ, irrelevant of heat transfer at constant pressure.

iv) $\Delta U_p = q_p + w = -45.8 + w \quad \Delta U_v = -46.9$ kJ

Difference = work done = -46.9 – (-45.8) = -1.1 kJ

7a) A state function is a property whose value depends solely on the state of the system. Its value is independent of the path used to achieve that state.

b) The opposite of a state function is a path function. A path function is a property whose value can vary dependent on the path used to reach a certain state.

ci) Path function

ii) State function

iii) State function

iv) Path function

8a) An intensive property is independent of the mass of the system. An extensive property is dependent on the mass of the system.

bi) Intensive

ii) Intensive

iii) Extensive

iv) Intensive

v) Extensive

iv) Extensive

9a) $w = -P_{ex}\Delta V$

b) $\Delta U = q - P_{ex}\Delta V$

c) -102 J

10)

Path A: Step 1, no ΔV thus no work done.

Step 2, $w = -P_{ex}\,\Delta V$ = -1.89 x (20.10-13.05) = -13.32 L atm = -1.35 kJ

Path B: $w = -nRT\ln(\frac{V_{final}}{V_{initial}})$

w = - 1.45 mol x 8.314 J K^{-1} mol^{-1} x 273 K x ln (20.10 / 13.05) = -1.42 kJ

Calorimetry

Question 1

The heat released or absorbed in chemical reactions can be monitored by measuring the temperature change that results. Such reactions are carried out in a "calorimeter". Give the expression which relates the heat energy transferred to the calorimeter, q_{cal}, to the observed change in temperature, ΔT.

Question 2

1.0 g octane was burned in a calorimeter with a heat capacity of 994 J K^{-1}. The temperature of the calorimeter rose by 4.88˚C. Calculate the heat energy released by the octane.

Question 3

a) Explain how the specific heat capacity, C_s, of a substance is related to its heat capacity.

b) Define specific heat capacity, C_s, and heat capacity, C, as intensive or extensive properties.

Worked Example 1

Calculation of the specific heat capacity of a metal by calorimetry:

A piece of copper, mass 30.0 g, was heated to 90°C and placed into a calorimeter of heat capacity 20 J °C $^{-1}$ containing 100 ml water at 20°C. The temperature of the calorimeter and water increased to 22°C. Calculate the specific heat capacity of the copper.

Answer

We know energy is transferred as heat when the copper cools, so we can write the equality:

Heat lost by copper = Heat gained by calorimeter + Heat gained by water

Heat change = m Cs ΔT, thus the equation becomes:

$$m_{Cu}\ Cs_{Cu}\ \Delta T_{Cu} = \Delta T_{Cal}\ C_{Cal} + m_{Water}\ Cs_{Water}\ \Delta T_{Water}$$

Everything ended up at 22°C thus we find the values of ΔT as follows:

$\Delta T_{Cu} = 90-22 = 68^\circ C$

$\Delta T_{Cal} = 22-20 = 2^\circ C$

$\Delta T_{water} = 22-20 = 2^\circ C$

And thus substituting these values (and those given in the question) into the overall equation:

$$30.0 \times Cs_{Cu} \times 68 = (20 \times 2) + (100 \times 4.184 \times 2)$$

$$Cs_{Cu} = 0.430\ J\ K^{-1}\ g^{-1}$$

Question 4

A piece of iron of mass 200g was heated from 20°C to 100°C and dropped in a calorimeter containing 300 ml water, originally at 20°C. The temperature of the water and the calorimeter rose to 25°C. Calculate Cs_{Fe}, given that the heat capacity of the calorimeter = 30 J K^{-1}, and the specific heat capacity of water = 4.184 J $K^{-1}g^{-1}$.

Question 5

Define the following terms:

i) Standard heat of formation of a compound, $\Delta H^{\ominus}_f$

ii) Standard heat of combustion of a compound, $\Delta H^{\ominus}_c$

iii) Standard heat of reaction of a compound, $\Delta H^{\ominus}_r$

iv) Standard heat of atomisation, $\Delta H^{\ominus}_a$

v) Mean bond enthalpy, ΔH_B

Question 6

a) If 80 kJ of heat are supplied to a calorimeter and the temperature changes by +8.40°C, calculate the heat capacity of the calorimeter.

b) If a chemical reaction is studied in the calorimeter and $\Delta T = +5.2°C$, calculate the heat, q, released. Is the reaction exothermic or endothermic?

Question 7

When 0.1016 g of octane, C_8H_{18}, is burned in a calorimeter with a heat capacity of 400 J K^{-1} and is surrounded by 1500 cm^3 water, the temperature of the calorimeter and water rose by 4.88°C. What is the enthalpy of reaction for the combustion of octane?

Question 8

If an electrical heater operating at 1.5 V supplies 10.6 A of current for 10 minutes, how much heat is given out?

Question 9

In an experiment to determine the standard enthalpy of combustion of propan-1-ol a 0.60 g sample of the liquid was completely burnt in a calorimeter containing 0.5 dm^3 water at 25˚C. The temperature of the calorimeter and its contents increased to 33.4˚C. The heat capacity of the calorimeter was determined independently by electrical measurements. At a voltage of 5 V a current of 1 A resulted in a 5˚C rise in temperature after 5 minutes (Q(J) = I(A) x V(V) x t(s))
Calculate the standard molar enthalpy of combustion of propan-1-ol.
(Heat capacity of water = 4.20 J K^{-1} g^{-1})

Calorimetry Answers

1) $q_{cal} = C_{cal}\,\Delta T$ (where C_{cal} = heat capacity of the calorimeter)

2) q_{cal} = 4851J = 4.85 kJ

3a) C_s is the heat capacity *per gram (or kilogram) mass* of a substance
i.e. $C_s \times \text{Mass} = C$

b) C is (as shown in the above equation) is dependent upon mass, and so is extensive. C_s is intensive as it has a specific value regardless of the amount of substance present.

4) Heat lost by the iron = Heat gained by the water + heat gained by calorimeter

$$m_{Fe} \times Cs_{Fe} \times \Delta T_{Fe} = m_{water} \times Cs_{water} \times \Delta T_{water} + C_{cal} \times \Delta T_{cal}$$

$$200\text{ g} \times Cs_{Fe} \times 75\text{ K} = 300\text{ g} \times 4.184\text{ J g}^{-1}\text{ K}^{-1} \times 5\text{ K} + 30\text{J K}^{-1} \times 5\text{ K}$$

$$Cs_{Fe} = 6426\text{ J}/15000\text{ g K}$$

$$Cs_{Fe} = 0.428\text{ J g}^{-1}\text{K}^{-1}$$

5i) The standard heat of formation of a compound is the enthalpy change on forming one mole of a compound from its elemental reactants in their standard states under standard conditions.

ii) The standard heat of combustion of a compound is the enthalpy change on completely combusting one mole of compound in excess oxygen under standard conditions.

iii) The standard heat of reaction is the enthalpy change when reactants in their standard states change to products in their standard states.

iv) The standard heat of atomisation is the enthalpy change upon converting one mole of a species' molecules in their standard state to individual gaseous particles with no interatomic interactions at a specified temperature and atmospheric pressure

v) Mean bond enthalpy is the average molar enthalpy change accompanying the dissociation of a given type of bond. Average bond enthalpies are an average over all different environments of the bond.

6a) $q = C_{cal} \times \Delta T$

therefore $C_{cal} = q/\Delta T = 80 \text{ kJ}/ 8.40 \text{ K} = 9.5 \text{ kJ K}^{-1}$

b) $q = C_{cal} \times \Delta T = 9.5 \text{ kJ K}^{-1} \times 5.2 \text{ K}$

$q = 49.5$ kJ (exothermic)

7) q lost by octane = q gained by water and calorimeter

$= m_{water} \times Cs_{water} \times \Delta T_{water} + C_{cal} \times \Delta T_{cal}$

$= 1500 \text{ g} \times 4.184 \text{ J g}^{-1} \text{ K}^{-1} \times 4.88 \text{ K} + 400 \text{ J K}^{-1} \times 4.88 \text{ K}$

= 30627 J + 1952 J

= 32579 J

Heat energy lost by burning 0.1016 g octane = 32579 J

1 mole octane (C_8H_{18}) = 114 g mol^{-1}

Therefore no. moles octane in 0.1016g = 0.1016 g/ 114 g mol^{-1} = 8.9×10^{-4} mol

8.9×10^{-4} moles octane releases 32579 J heat

Therefore 1 mole octane releases 32579 J/8.9×10^{-4} mol = 3660.6×10^{4} J

= 36,606 kJ

8) Electrical work done, Q = I x V x t (I = current (A), V = voltage (V), t = time (s))

Q = 10.6 A x 1.5 V x 600 s = 9.54 kJ

9) Q(J) = I(A) x V(V) x t(s)

= 1 A x 5 V x 5 x 60 s

= 1.5 kJ

1.5 kJ heat energy results in a 5 K rise in temperature of the calorimeter

Therefore a 1 K rise in temperature results from 1.5 kJ/ 5 = 0.3 kJ heat energy

Therefore $C_{cal} = 0.3 \text{ kJ K}^{-1}$

q lost by propan-1-ol = q gained by water and calorimeter

$= 500 \text{ g} \times 4.184 \text{ J g}^{-1} \text{ K}^{-1} \times (33.4 – 25.0) \text{ K} + 300 \text{ J K}^{-1} \times 8.4 \text{ K}$

= (17572.8 + 2520) J = 20.1 kJ

Therefore 0.60 g propan-1-ol on combustion releases 20.1 kJ heat energy

1 mole propan-1-ol = 60 g

Therefore 0.6 g is equivalent to 0.6 g / 60 g mol^{-1} = 0.01 mol

0.01 mole releases 20.1 kJ

Therefore 1 mol releases 20.1kJ/0.01 = 2010 kJ

Molar enthalpy of combustion of propan-1-ol = 2010 kJ mol^{-1}

Enthalpy and Hess' Law

Question 1

The enthalpy of a system is defined as the enthalpy change at constant pressure and can be defined as:

$$H = U + PV$$

The *change in* enthalpy, ΔH, can therefore be derived as:

$$\Delta H = \Delta U + P\Delta V$$

Use the first law of thermodynamics to show that the enthalpy change constant pressure for an open system, ΔH, is equal to the heat transferred during a reaction, q.

Worked Example 1 – Using Hess' Law

Calculate the standard enthalpy of combustion of cyclopropane, C_3H_6, given the following data:
Enthalpy of formation of cyclopropane, $\Delta H_f^{\ominus} = +53.3\ \text{kJ mol}^{-1}$
Enthalpy of combustion of carbon (graphite), $\Delta H_c^{\ominus}(C_{(gr)}) = -393.5\ \text{kJ mol}^{-1}$
Enthalpy of combustion of hydrogen, $\Delta H_c^{\ominus}(H_{2\,(g)}) = -285.8\ \text{kJ mol}^{-1}$

Answer

Firstly, we write down the chemical reaction for which we want the enthalpy change.

$$C_3H_6\,(gr) + 4\tfrac{1}{2}\,O_2\,(g) \xrightarrow{\Delta H_r} 3CO_2\,(g) + 3H_2O\,(g)$$

where ΔH_r is the enthalpy change we want
We are told the enthalpy of formation of cyclopropane in the question, so we add this formation in as a third point on our Hess' Law triangle:

$$\begin{tikzcd}
C_3H_6\,(g) + 4\tfrac{1}{2}\,O_2\,(g) \arrow[rr, "\Delta H_r"] & & 3CO_2\,(g) + 3H_2O\,(g) \\
& 3C\,(gr) + 3H_2\,(g) + 4\tfrac{1}{2}\,O_2\,(g) \arrow[ul, "\Delta H_f^{\ominus}"] &
\end{tikzcd}$$

We then complete the Hess' Law triangle by incorporating the information about the enthalpies of combustion of carbon (graphite) and hydrogen:

$$\begin{tikzcd}
C_3H_6\,(g) + 4\tfrac{1}{2}\,O_2\,(g) \arrow[rr, "\Delta H_r"] & & 3CO_2\,(g) + 3H_2O\,(g) \\
& 3C\,(gr) + 3H_2\,(g) + 4\tfrac{1}{2}\,O_2\,(g) \arrow[ul, "\Delta H_f^{\ominus}"] \arrow[ur, "3x\ \Delta H_c^{\ominus}(\ C_{(gr)}) + 3x\ \Delta H_c^{\ominus}(\ H_{2\,(g)})"'] &
\end{tikzcd}$$

Applying Hess' Law, the enthalpies of combustion of 3 moles of C (graphite) and 3 moles of H_2 minus the enthalpy change of formation of C_3H_6 is equal to the enthalpy change of combustion of C_3H_6:

$$\Delta H_r \quad = \Delta Hc^{\ominus}(C_3H_6) = 3x\Delta H_c^{\ominus}(\ C_{(gr)}) + 3x\Delta H_c^{\ominus}(\ H_{2\,(g)}) - \Delta H_f^{\ominus}(C_3H_6)$$

$= (3\text{x} -393.5) + (3\text{x} -285.8) – 53.3$
$= -2090.3 \text{ kJ mol}^{-1}$

Question 2

Given the following reaction enthalpies:

$2P\ (s) + 3Cl_2\ (g) \rightarrow 2PCl_3\ (g)\ \Delta H = -574 \text{ kJ mol}^{-1}$
$2P\ (s) + 5Cl_2\ (g) \rightarrow 2PCl_5\ (l)\ \ \Delta H = -887 \text{ kJ mol}^{-1}$

Calculate the enthalpy change for the reaction:

$PCl_3\ (g) + Cl_2\ (g) \rightarrow PCl_5\ (l)$

Question 3

a) Calculate the standard enthalpy of formation of propane, C_3H_8, from the data below:

$H_2\ (g) + ½O_2\ (g) \rightarrow H_2O\ (l) \qquad \Delta H = -286 \text{ kJ mol}^{-1}$
$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g) \qquad \Delta H = -394 \text{ kJ mol}^{-1}$
$C_3H_8 + 5O_2\ (g) \rightarrow 3CO_2\ (g) + 4H_2O\ (l) \qquad \Delta H^\circ = -2220 \text{ kJ mol}^{-1}$

b) What is the enthalpy change upon burning 1.00 m^3 of propane gas, measured at 1.00 atm and 298 K when $V_m = 24 \text{ dm}^3 \text{ mol}^{-1}$

Question 4

What is the standard enthalpy change for the following reaction?

$2SO_2\ (g) + O_2\ (g) \rightarrow 2SO_3\ (g)$

DATA:
$\Delta H_c\ (S_8\ (s)) = -3166 \text{ kJ mol}^{-1}$ when $SO_3\ (g)$ is produced
and $\Delta H_c\ (S_8\ (s)) = -2374 \text{ kJ mol}^{-1}$ when $SO_2\ (g)$ is the product.

Question 5

Given the following data:

$H_2\ (g) + F_2\ (g) \rightarrow 2HF\ (g)$ ΔH = -537 kJ mol^{-1}
$C\ (s) + 2F_2\ (g) \rightarrow CF_4\ (g)$ ΔH = -680 kJ mol^{-1}
$2C\ (s) + 2H_2\ (g) \rightarrow C_2H_4\ (g)$ ΔH = +52.3 kJ mol^{-1}

Calculate the enthalpy change for the fluorination of ethene:

$C_2H_4\ (g) + 6F_2\ (g) \rightarrow 2CF_4\ (g) + 4HF\ (g)$

Question 6

By forming a Hess' Law triangle, find the enthalpy of formation of acetone, C_3H_6O:

$C_3H_6O\ (l) + 4O_2\ (g) \rightarrow 3CO_2\ (g) + 3H_2O\ (l)$ ΔH_c = -1790 kJ mol^{-1}
$\Delta H_f\ (CO_2\ (g))$ = -393.5 kJ mol^{-1}
$\Delta H_f\ (H_2O\ (l))$ = -285.83 kJ mol^{-1}

Question 7

During the Apollo 11 project the engines of the lunar module used methylhydrazine, CH_3NHNH_2, and dinitrogen tetroxide, N_2O_4. Given the following standard heats of formation, calculate the enthalpy change for the reaction:

$4CH_3NHNH_2\ (l) + 5N_2O_4\ (l) \rightarrow 4CO_2\ (g) + 12H_2O\ (l) + 9N_2\ (g)$

DATA:

$\Delta H_f^\circ\ (CH_3NHNH_2\ (l))$ = +53 kJ mol^{-1} $\Delta H_f^\circ\ (CO_2\ (g))$ = -393 kJ mol^{-1}
$\Delta H_f^\circ\ (N_2O_4\ (l))$ = -20 kJ mol^{-1} $\Delta H_f^\circ\ (H_2O\ (l))$ = -286 kJ mol^{-1}

Question 8

a) State the First Law of Thermodynamics defining any quantities used.
b) State Hess' Law
c) Calculate the standard enthalpy change of formation of butane, C_4H_{10} (*g*), from the following data:

$H_2\ (g) + ½O_2\ (g) \rightarrow H_2O\ (l)$	$\Delta H = -286\ kJ\ mol^{-1}$
$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)$	$\Delta H = -394\ kJ\ mol^{-1}$
$C_4H_{10}\ (g) + 13/2O_2\ (g) \rightarrow 4CO_2 + 5H_2O\ (l)$	$\Delta H = -2877\ kJ\ mol^{-1}$

d) How much heat is released by burning 1.00 m^3 of butane gas, measured at 1.00 atm and 298 K, when $V_m = 24\ dm^3\ mol^{-1}$

Enthalpy and Hess' Law Answers

1) $\Delta H = \Delta U + P\Delta V$

The first law states that: $\Delta U = q + w$

Substituting in for ΔU gives us:

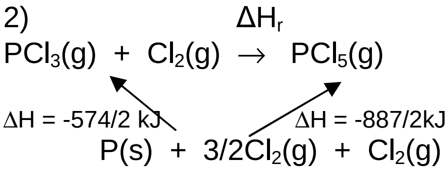
$\Delta H = q + w + P\Delta V$

The expansion work done, w, at constant pressure, P, is given by: $w = -P\Delta V$

Thus $\Delta H = q - P\Delta V + P\Delta V$

$\Delta H = q$ (at constant pressure)

2)

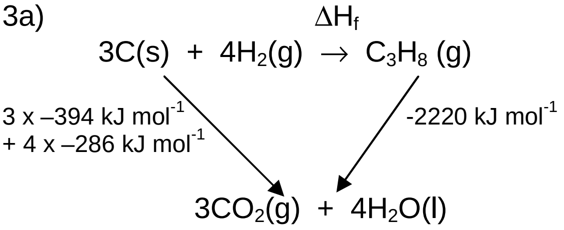


Applying Hess' Law:

$-574/2\ \text{kJ} + \Delta H_r = -887/2\ \text{kJ}$

$\Delta H_r = -443.5\ \text{kJ mol}^{-1} + 287\ \text{kJ mol}^{-1} = -156.5\ \text{kJ mol}^{-1}$

3a)



Applying Hess' Law:

$\Delta H_r + (-2220)\ \text{kJ mol}^{-1} = 3 \times -394\ \text{kJ mol}^{-1} + 4 \times -286\ \text{kJ mol}^{-1}$

$\Delta Hr = -1182\ \text{kJ mol}^{-1} + -1144\ \text{kJ mol}^{-1} + 2220\ \text{kJ mol}^{-1} = -106\ \text{kJ mol}^{-1}$

b)

1 mole propane (C_3H_8) releases 2220 kJ mol^{-1}

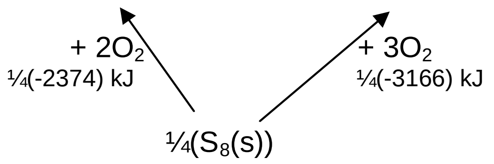
1 mole propane has volume of 24 dm^3 at 1.0 atm and 298 K

1 dm^3 releases $-2220/24\ \text{dm}^3 = -92.5\ \text{kJ mol}^{-1}$

Therefore 1 m^3 releases -92.5×10^3 kJ = -92.5 MJ

4)

$$2SO_2(g) + O_2(g) \xrightarrow{\Delta H_r} 2SO_3(g)$$



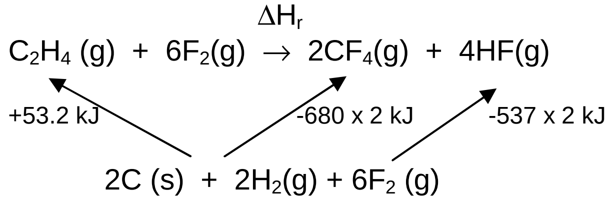
Applying Hess' Law:

¼(-2374) kJ + ΔH_r = ¼(-3166) kJ

ΔH_r = -791.5 kJ + 593.5 kJ

ΔH_r = -198 kJ mol^{-1}

5)



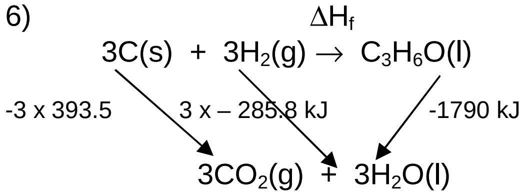
Applying Hess' Law:

+53.2 kJ + ΔH_r = -680 x 2 kJ - 537 x 2 kJ

ΔH_r = -1360 kJ – 1074 kJ – 53.2 kJ

ΔH_r = -2.49 MJ mol^{-1}

6)



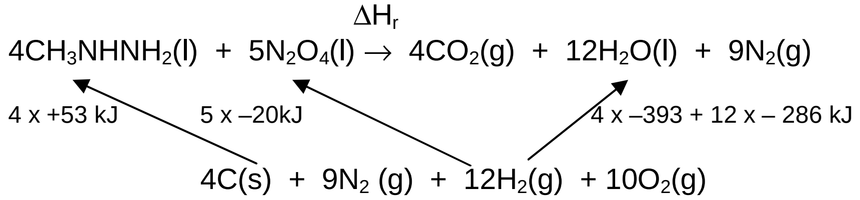
Applying Hess' Law:

ΔH_f - 1790 kJ = 3 x -393.5 kJ + 3 x – 285.5 kJ

ΔH_f = -1180.5 - 857.4 + 1790 kJ

ΔH_f = -248 kJ

7)



Applying Hess' Law:

ΔH_r + 4 x +53 + 5 x 20 kJ = 4 x –393 + 12 x –286 kJ

ΔH_r = -1572 - 3432 – 312 kJ

ΔH_r = -5316 kJ

8a) The internal energy of an isolated system remains constant ($\Delta U = 0$),
The change in internal energy of a system is equivalent to the heat absorbed (q) plus the work done on/by the system (w.) The heat transferred is due to temperature differences between the system and its surroundings. The work done on/by a system is due to any change in volume of the system ($w = P\Delta V$) which gives a measure of the internal energy at constant pressure. At constant volume, $\Delta U = q$.

$$\Delta U = q + w$$

b) Hess' Law states that the enthalpy change for a reaction is the sum of any number of enthalpy changes that result in the same initial and final components and conditions.

c) $\Delta H_f = -129$ kJ mol^{-1}
d) $\Delta H = 5.38$ MJ

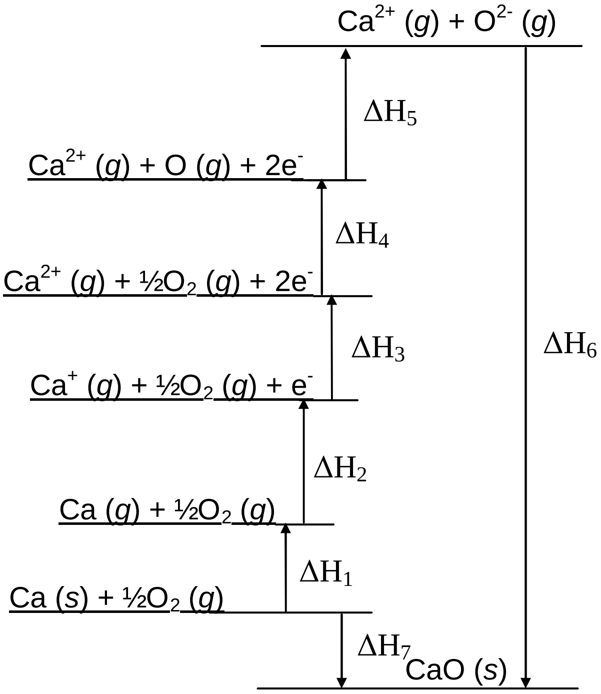
The Born Haber Cycle

Question 1

Write chemical equations which describe the following terms:
a) The enthalpy of formation of calcium oxide
b) The enthalpy of atomisation of calcium
c) The 1st ionisation energy of calcium
d) The 2nd ionisation energy of calcium
e) The enthalpy of atomisation of oxygen
f) The bond enthalpy for oxygen
g) The first electron affinity of oxygen
h) The second electron affinity of oxygen
i) The lattice enthalpy of calcium oxide

Question 2

Identify each of the steps on the diagram below. Some steps may be combinations or reiterations of the terms in question 1 (above.)



Question 3

a) Given the following data, calculate the value of ΔH_5 on the diagram above.
ΔH_1 = +193 kJ mol^{-1}, ΔH_2 = +590 kJ mol^{-1}, ΔH_3 = +1150 kJ mol^{-1}, ΔH_4 = +248 kJ mol^{-1}, ΔH_6 = -3513 kJ mol^{-1}, ΔH_7 = -635 kJ mol^{-1}
b) Use the value of ΔH_5 you have calculated to obtain the first electron affinity of oxygen, given that the second electron affinity of oxygen is +844 kJ mol^{-1}

Question 4

a) Explain why the first electron affinity of oxygen is exothermic whilst the second electron affinity is endothermic.
b) Explain the difference between the terms in 1(e) and 1(f), above.
c) Would the value of ΔH_2 for Mg be larger or smaller than that for Ca?
d) How would you expect the value of the lattice enthalpy to vary for the series MgO, CaO, SrO, BaO?
e) Would you expect the value of the lattice enthalpy for $CaCl_2$ to be greater or smaller than that of CaO?

The Born Haber Cycle Answers

1a) $Ca\ (s) + \frac{1}{2}O_2\ (g) \rightarrow CaO\ (s)$

b) $Ca\ (s) \rightarrow Ca\ (g)$

c) $Ca\ (g) \rightarrow Ca^+\ (g) + e^-$

d) $Ca^+\ (g) \rightarrow Ca^{2+}\ (g) + e^-$

e) $\frac{1}{2}O_2\ (g) \rightarrow O\ (g)$

f) $O_2\ (g) \rightarrow 2O\ (g)$

g) $O\ (g) + e^- \rightarrow O^-\ (g)$

h) $O^-\ (g) + e^- \rightarrow O^{2-}\ (g)$

i) $CaO\ (s) \rightarrow Ca^{2+}\ (g) + O^{2-}\ (g)$

2)

$\Delta H_1 = \Delta H_a\ [Ca]$

$\Delta H_2 = \Delta H_{IE}\ [Ca]$

$\Delta H_3 = \Delta H_{IE}\ [Ca^+]$

$\Delta H_4 = \Delta H_a\ [O_2]$

$\Delta H_5 = \Delta H_{EA}\ [O] + \Delta H_{EA}\ [O^-]$

$\Delta H_6 = -\ \Delta H_{lat}\ [CaO]$

$\Delta H_7 = \Delta H_f\ [CaO]$

3a) $\Delta H_5 = \Delta H_7 - \Delta H_1 - \Delta H_2 - \Delta H_3 - \Delta H_4 - \Delta H_6$

$\Delta H_5 = -635 - 193 - 590 - 1150 - 248 + 3513$

$\Delta H_5 = +\ 697\ \text{kJ mol}^{-1}$

b) $\Delta H_5 = \Delta H_{EA}\ [O] + \Delta H_{EA}\ [O^-]$

Thus $\Delta H_{EA}\ [O] = -147\ \text{kJ mol}^{-1}$

4a) In the first electron affinity (EA) we are adding an electron to a neutral atom, and the electronic configuration of atomic oxygen means that it is a thermodynamically favourable process. However, in the second EA we are attempting to add an electron (a negatively charged particle) to O^- (*g*) (a negatively charged ion.) Elementary physics tells us this is energetically unfavourable, and hence it requires energy (is endothermic.)

b) The enthalpy of atomisation is the energy required to atomise *one atom* of oxygen from its elemental form. The bond enthalpy is the energy required to break the oxygen-oxygen double bond. As oxygen is a diatomic molecule, the bond enthalpy is twice the atomisation energy (as breaking the bond forms *two atoms* of oxygen.)

c) It would be larger (more endothermic) for magnesium than for calcium as magnesium is in the period above calcium, and thus calcium has an extra full shell of electrons between the valence electrons and the nucleus. This means these electrons are more shielded than the magnesium and are further from the nucleus than in magnesium, meaning they're less well held. This means that calcium is easier to ionise than magnesium, and thus has a lower ionisation energy.

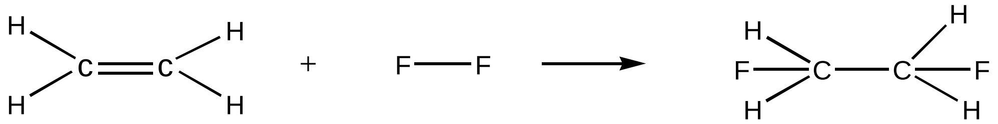
d) It will decrease along the series. This is because the ionic radius of the cations increases along the series, which means they will form less well-structured lattices with the smaller oxygen anion, and will hence have lower lattice enthalpies.

e) $CaCl_2$ will have a lower lattice enthalpy than CaO, because the chloride anion (Cl^-) has a lower charge and larger ionic radius than the oxide anion (O^{2-}).

Bond Enthalpies

Worked Example – Bond enthalpies

Estimate the standard enthalpy of reaction in which 1 mole of gaseous ethene, C_2H_4 (*g*), reacts with gaseous fluorine, F_2 (*g*), to form gaseous 1,2 difluoroethane, $C_2H_2F_2$ (*g*).



Bond enthalpies: C=C $= 612\ \text{kJ mol}^{-1}$
F–F $= 158\ \text{kJ mol}^{-1}$
C–F $= 484\ \text{kJ mol}^{-1}$
C–C $= 348\ \text{kJ mol}^{-1}$

Answer

We are going to use the equation:
ΔH_f° *= Enthalpy required to break bonds– Enthalpy released on bond formation*

So to find the enthalpies of bonds broken (energy required):
1 x C=C = + 612 kJ mol^{-1}
1 x F–F = + 158 kJ mol^{-1}
TOTAL = + 770 kJ mol^{-1}
And to find the enthalpies of bonds formed (energy produced):
2 x C–F = -2 x 484 = -968 kJ mol^{-1}
1 x C–C = -348 kJ mol^{-1}
TOTAL = -1316 kJ mol^{-1}
So using the equation:
ΔH_f° *= Enthalpy required to break bonds– Enthalpy released on bond formation*
= (770) – (1316)
= -546 kJ mol^{-1}

Question 1

Hydrazine, N_2H_4 (*g*), is often used as rocket fuel. It reacts exothermically with O_2 (*g*) forming gaseous products only.

$$N_2H_4\,(g) + O_2\,(g) \rightarrow N_2\,(g) + 2H_2O\,(g) \qquad \Delta H^{\circ} = -622\ \text{kJmol}^{-1}$$

It is possible that hydrazine/fluorine mixtures may be more exothermic than hydrazine/oxygen, and hence provide more thrust. Comment on the validity of this hypothesis by calculating ΔH for the reaction of hydrazine with fluorine given the following average bond enthalpies:

ΔH_B (N–N) = 163 kJ mol^{-1} ΔH_B (N≡N) = 945 kJ mol^{-1}
ΔH_B (N–H) = 390 kJ mol^{-1} ΔH_B (H–F) = 565 kJ mol^{-1}
ΔH_B (F–F) = 158 kJ mol^{-1}

Question 2

a) Define the term standard enthalpy of formation as applied to gaseous hydrazine, N_2H_4 (*g*).
b) Calculate the standard enthalpy of combustion of gaseous hydrazine (to liquid water and gaseous nitrogen) given that the standard enthalpies of formation of H_2O (*l*) and N_2H_4 (*g*) are –286 and +95 kJ mol^{-1} respectively.
c) How much energy is released in the complete combustion of 1.00 g of gaseous hydrazine?
d) Calculate the standard enthalpy of formation of gaseous hydrazine given the following bond enthalpies (in kJ mol^{-1}):
ΔH_B (H–H) = 436; ΔH_B (N–N) = 163; ΔH_B ($N\equiv N$) = 944; ΔH_B (N–H) = 388

Question 3

Use the average bond enthalpy data to calculate the enthalpy of atomisation of benzene, C_6H_6:
a) Assuming it has 3 C–C and 3 C=C bonds.
b) Assuming it has 6 C⎓C partial double bonds.
c) Account for the difference between your answers for a) and b)
ΔH_B (C–H) = 412 kJ mol^{-1}; ΔH_B (C=C) = 612 kJ mol^{-1};
ΔH_B (C–C) = 348 kJ mol^{-1}; ΔH_B (C⎓C) = 518 kJ mol^{-1}.

Bond Enthalpies Answers

1)

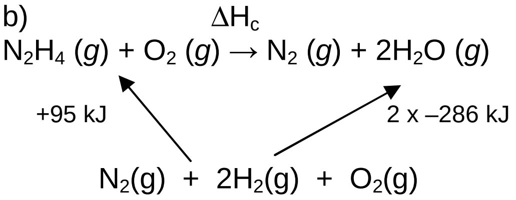
Total bonds broken:	Total bonds formed
1 x N-N = +163 kJ	1 x N=N = -945 kJ
4 x N-H = +1560 kJ	4 x H-F = -2260 kJ
2 x F-F = +316 kJ	
Total = + 2039 kJ	Total = -3205 kJ

Difference = -1166 kJ

ΔH = -1166 kJ mol^{-1} thus more exothermic than hydrazine/oxygen mixtures, so possibly a better fuel

2a) It is the enthalpy change when 1 mole of gaseous hydrazine is formed from its constituent elements in their standard states at a specific temperature and atmospheric pressure.

b)



Applying Hess' Law:

$+\ 95\ \text{kJ}\ +\ \Delta H_c\ = 2 \times -286\ \text{kJ}$

$\Delta H_c = -572\ \text{kJ}\ -\ 95\ \text{kJ}\ = -667\ \text{kJ}$

c) Combustion of 1 mole hydrazine releases 667 kJ

1 mole hydrazine = 32 g

Therefore combustion of 1 g releases 667 kJ/32

ΔH = 20.84 kJ

d) For formation of hydrazine:

$N\text{-}N + 2H\text{-}H \rightarrow H_2NNH_2$

Total bonds broken	Total bonds formed
1 x N≡N = +944 kJ mol^{-1}	1 x N-N = -163 kJ mol^{-1}
2 x H-H = 2 x + 436 kJ mol^{-1}	4 x N-H = 4 x -388 kJ mol^{-1}
Total energy required = +1816 kJ mol^{-1}	Energy released = -1715 kJ mol^{-1}

Difference = +101 kJ mol^{-1}

Therefore theoretical ΔH_f = +101 kJ mol^{-1}

3a) 3 x (C-C) = 3 x +348 kJ mol^{-1}

3 x (C=C) = 3 x + 612 kJ mol^{-1}

6 x (C-H) = 6 x +412 kJ mol^{-1}

Total ΔH_{at} = +5352 kJ mol^{-1}

b) 6 x (C$\overset{\cdots}{-}$C) = 6 x +518 kJ mol^{-1}

6 x (C-H) = 6 x +412 kJ mol^{-1}

Total ΔH_{at} = +5580 kJ mol^{-1}

c) The difference is assigned to the fact that in b) the electronic delocalisation across the benzene ring gives the structure additional stability, hence a greater amount of energy required to atomise it.

The Second Law of Thermodynamics

Question 1

When applied at constant temperature, the second law of thermodynamics gives us the following relationship:

$$\Delta S = \frac{q_{rev}}{T}$$

a) Define and give the standard units of:

i) ΔS

ii) q_{rev}

iii) T

b) Use the above relationship to calculate the change in entropy when a large block of ice loses 50 J of heat energy at 0˚C in a freezer. Comment on the sign of the entropy change.

Question 2

a) Using the following standard entropy values, calculate the standard entropy changes for:
i) $CaCO_3$ (*s*) → CaO (*s*) + CO_2 (*g*)

ii) H_2 (*g*) + ½O_2 (*g*) → H_2O (*l*)

b) Comment on the sign of ΔS° with reference to the states of the reactants and products.

DATA

Substance	**S°/ J K^{-1} mol^{-1}**	**Substance**	**S°/ J K^{-1} mol^{-1}**
$CaCO_3$	92.9	H_2	131
CaO	40	O_2	205
CO_2	214	H_2O	69.9

Question 3 – Proof

a) Show that when a gas is heated at constant volume, from temperature T_1 to temperature T_2, the increase in entropy of the gas, ΔS, is given by:

$$\Delta S = C_v \ln\frac{T_2}{T_1}$$

Where C_v is the specific heat capacity of the gas at constant volume.

b) What is the entropy change if the heating is done at constant pressure (where C_p is the specific heat capacity)?

Question 4

Calculate the entropy change on heating 1 mole of argon from 298K to 500K.
C_p (Ar) = 20.8 J K^{-1} mol^{-1}

Question 5

Show that when a gas expands isothermally from volume V_1 to volume V_2, the entropy change can be expressed as:

$$\Delta S = n\,R \ln\frac{V_2}{V_1}$$

Where n is the number of moles and R is the gas constant.

Question 6

Calculate the entropy change on one mole of gas expanding from 89.1 cm^3 to 1dm^3.
($R = 8.3145$ J K^{-1} mol^{-1})

Question 7

Calculate the entropy change when the pressure of 2.50 moles of gaseous neon is increased from 10.00 bar to 50.00 bar

Question 8

Calculate the molar entropy change when gaseous nitrogen expands to 8 times its initial volume.

The Second Law of Thermodynamics – Answers

1a)

i) ΔS = change in entropy (JK^{-1})

ii) q_{rev} = reversible energy change (J)

iii) T = temperature of surroundings and system (K)

b) $\Delta S = -50\ kJ/273\ K = -0.18\ J\ K^{-1}$, negative implies an increase in order as the ice cools, which is logical.

2a)

i) ΔS° = S(products)-S(reactants) = ((40+214)-92.9) $J\ K^{-1}\ mol^{-1}$ = 161 $J\ K^{-1}\ mol^{-1}$

ii) ΔS° = S(products)-S(reactants) = (69.9-(131 + 0.5 x 205)) $J\ K^{-1}mol^{-1}$ = -164 $J\ K^{-1}\ mol^{-1}$

b) in (i) a gas is produced from a solid hence disorder, and entropy, increases.

In (ii) a liquid is produced from two gases hence disorder decreases and entropy decreases.

3) Proof –

Differential definition of entropy:

$dS = d(q_{rev}) / T$

$d(q_{rev}) = C_v\ dT$, by definition of heat capacity.

Substituting in for $d(q_{rev})$ yields:

$dS = C_v\ dT / T$,

so between the limits T_1 and T_2…

$$\Delta S = C_v \int_{T_1}^{T_2} \frac{1}{T}\, dT = C_v \ln\left[\frac{T_2}{T_1}\right]$$

b) If we keep pressure constant and use C_p we yield:

$d(q_{rev}) = C_p\ dT$

thus our final entropy change is given by:

$$\Delta S = C_p \int_{T_1}^{T_2} \tfrac{1}{T}\, dT = C_p \ln\left[\frac{T_2}{T_1}\right]$$

4) Using

$$\Delta S = C_p \ln\left[\frac{T_2}{T_1}\right]$$

$\Delta S = 20.8\ \text{J K}^{-1}\ \text{mol}^{-1} \times \ln(500/298) = 10.8\ \text{J K}^{-1}\ \text{mol}^{-1}$

5) From the first law, for a reversible, isothermal expansions:

$\Delta U = q_{rev} + w_{rev} = 0$ (as it's isothermal)

Thus $q_{rev} = -w_{rev}$

The work done in an isothermal, reversible expansion is given by:

$w_{rev} = -nRT \ln(V_2 / V_1)$

$\Delta S = q_{rev} / T$

$= -w_{rev} / T$

$= n R \ln(V_2 / V_1)$

6) $\Delta S = n R \ln(V_2 / V_1)$

$\Delta S = 1\text{mol} \times 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1} \times \ln(1000/89.1) = 20.1\ \text{J K}^{-1}$

7) $\Delta S = 2.5\ \text{mol} \times 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1} \times \ln(50.0/10.0) = .5\ \text{J K}^{-1}$

8) $\Delta S = 1\ \text{mol} \times 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1} \times \ln(8/1) = 17.3\ \text{J K}^{-1}\ \text{mol}^{-1}$

Gibbs Free Energy

Question 1

The free energy change for a process that occurs at constant temperature is given by:

$$\Delta G = \Delta H - T\Delta S$$

This expression is important as it allows us to determine whether a reaction is spontaneous. This means that at constant pressure and temperature, the direction of spontaneous change is towards lower free energy,
i.e. ΔG must be negative for spontaneous change.

Decide whether, given the parameters quoted, the following reactions will be spontaneous:
a) Enthalpy change exothermic, Entropy increases

b) Enthalpy change endothermic, Entropy increases, but $T\Delta S < \Delta H$

c) Enthalpy change endothermic, Entropy decreases

Question 2

a) Define the terms in the following equation:

$$\Delta G = \Delta H - T\Delta S$$

ΔG =

ΔS =

ΔH =

T =

b) State the values of ΔG for which a spontaneous process would be predicted.

c) What values of ΔH would permit spontaneous reaction if there was a decrease in entropy of the system?

d) If the reaction is spontaneous and endothermic, what can be said about the change in entropy?

e) Estimate the temperature at which it is thermodynamically possible for carbon to reduce iron (III) oxide by the endothermic reaction

$$2Fe_2O_3\,(s) + 3C\,(s) \rightarrow 4Fe\,(s) + 3CO_2\,(g) \qquad \Delta H = +467.9\ \text{kJ mol}^{-1}$$
$$\Delta S = 558.32\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Question 3

Determine ΔG_r for the reaction

$CH_4\,(g) + N_2\,(g) \rightarrow HCN\,(g) + NH_3\,(g)$

At 298K.

DATA:

	CH_4 (*g*)	N_2 (*g*)	HCN (*g*)	NH_3 (*g*)
ΔH_f / kJ mol^{-1}	-74.81	0	135	-46.11
S / J K^{-1} mol^{-1}	186.15	191.5	201.7	192.3

Question 4

For the reaction:

$SO_2Cl_2\,(l) \rightleftharpoons SO_2\,(g) + Cl_2\,(g)$

a) Would you expect ΔH° to be positive or negative?

b) Would you expect ΔS° to be positive or negative?

c) What can you say (if anything) about ΔG°?

Question 5

a) The water gas shift reaction provides a way to convert unwanted CO into H_2:

$$H_2O\ (g) + CO\ (g) \rightleftharpoons H_2\ (g) + CO_2\ (g)$$

i) Using the following data for free energies of formation, calculate ΔG° for the reaction at 298 K.

ii) Using the Vant Hoff Isotherm Equation calculate the equilibrium constant, *K*.

DATA

Substance	ΔG_f° / kJ mol^{-1}
H_2O (*g*)	-229
CO (*g*)	-137
H_2 (*g*)	0
CO_2 (*g*)	-395

b) Using the following data for ΔH_f° and S°, calculate the "breakeven temperature", T_{be}, at which $\Delta G = 0$. State any assumptions you make.

DATA

	H_2O (*g*)	CO (*g*)	H_2 (*g*)	CO_2 (*g*)
ΔH_f° / kJ mol^{-1}	-242	-111	0	-394
S° / J K^{-1} mol^{-1}	+189	+198	+131	+214

Gibbs Free Energy Answers

1a) ΔH = negative, $-T\Delta S$ = negative, thus ΔG = negative i.e. spontaneous

b) ΔH = positive, $-T\Delta S$ = negative, but $| T\Delta S | < \Delta H$, thus ΔG = positive i.e. not spontaneous

c) ΔH = positive, $-T\Delta S$ = positive, ΔG = positive i.e. not spontaneous

2a) ΔG = Gibbs free energy change

ΔH = Enthalpy change

T = Temperature (Kelvin)

ΔS = Entropy change

b) ΔG must be negative

c) Decrease in entropy $\Rightarrow$ ΔS is negative, thus $-T\Delta S$ is positive.

For a spontaneous reaction, ΔG is negative, thus $\Delta H < T\Delta S$ would permit spontaneity.

d) ΔH is positive, hence $T\Delta S > \Delta H$ to allow ΔG to be negative, thus ΔS must be positive.

e) ΔG changes sign when $T = \Delta H / \Delta S$

thus $T = 467{,}900 / 558.32 = 838\ \text{K}$

3) $\Delta H_f = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$

$= (135-46.11)\ \text{kJ mol}^{-1} - (-74.81 + 0)\ \text{kJ mol}^{-1}$

$= (88.89 + 74.81)\ \text{kJ mol}^{-1}$

$= 163.7\ \text{kJ mol}^{-1}$

$\Delta S = S_{\text{products}} - S_{\text{reactants}}$

$= (201.7 + 192.3)\ \text{J K}^{-1}\ \text{mol}^{-1} - (186.15 + 191.5)\ \text{J K}^{-1}\ \text{mol}^{-1}$

$= (394 - 377.65)\ \text{J K}^{-1}\ \text{mol}^{-1}$

$= 16.35\ \text{J K}^{-1}\ \text{mol}^{-1}$

$\Delta G_r = \Delta H - T\Delta S = (163.7\ \text{kJ mol}^{-1}) - (298\ \text{K}) \times (16.35\ \text{J K}^{-1}\ \text{mol}^{-1}) = 158.83\ \text{kJ mol}^{-1}$

4a) Positive (Dissociation generally favoured by increase in T)

b) Positive (Production of two moles of gas from one mole of gas)

c) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

At low temperatures, ΔH° dominates the equation and ΔG° is positive, favouring association.

At high temperatures, $T\Delta S^\circ$ dominates the equation and ΔG° is negative, favouring dissociation.

5a)

i) $\Delta G^\circ = -29\ \text{kJ mol}^{-1}$

ii) ln K = $-\Delta G^\circ / RT = 11.70$

$K = 1.21\text{x}10^5$

b)

$\Delta H^\circ = -41$ kJ mol^{-1}

$\Delta S^\circ = -42$ J K^{-1} mol^{-1}

At T_{be} $\Delta G = 0$ thus $\Delta H = T_{be}\Delta S$

Hence we see $T_{be} = \Delta H / \Delta S$

$= -41{,}000 / -42$

$= 976$ K

We have assumed that ΔH° and ΔS° don't vary with temperature.

Kinetics

Worked example 1

a) What is meant by rate of reaction?

For the reaction

$$A \rightarrow 2B$$

b) Give two equations for the average rate, in terms of change in concentration of reactants and products.
c) What is the relationship between the two rates of reaction?
d) What are the standard units of the rate?

Answers

a) The rate of reaction is a measure of how quickly reactants are converted to products. Hence it is either the rate of change of consumption of reactants or the rate of change of formation of products.

b) $\text{Rate} = -\Delta[A] / \Delta t$
$\text{Rate} = \Delta[B] / \Delta t$

c) $-\Delta[A] / \Delta t = \frac{1}{2}\,\Delta[B] / \Delta t$
d) Standard units are $\text{mol dm}^{-3}\text{s}^{-1}$

Question 1

In the combustion of methane

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g)$$

The rate of consumption of oxygen was found to be $-\Delta[O_2] / \Delta t = 0.2 \text{ mol s}^{-1}$

a) What is the average reaction rate with respect to combustion of methane?
b) What is the rate of production of gaseous CO_2?
c) If initially there were 10.00 mol of CH_4, how many moles of CH_4 would be present after 40 s?

Worked example 2

For the reaction

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

the rate is governed by the rate law

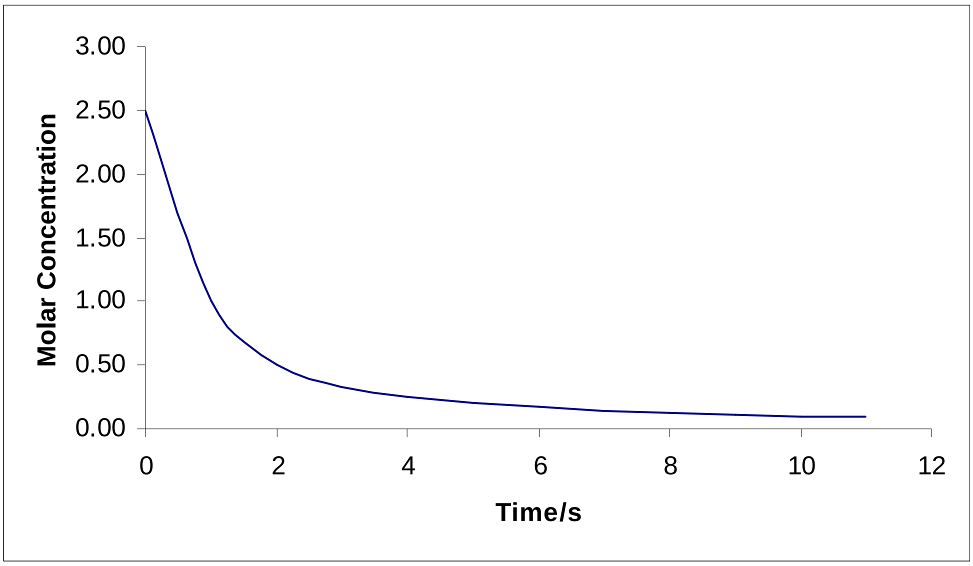
$$\text{Rate} = k\,[N_2O_5]$$

a) What is the order of reaction with respect to

i) N_2O_5
ii) NO_2
iii) O_2

b) What is the overall order of the reaction?

c) From the graph of molar concentration of N_2O_5 against time (s):



i) What was the initial concentration of N_2O_5?
ii) Use the graph to find the gradient and hence find the rate constant k stating its units.

Answers

a i) Order is power that $[N_2O_5]$ is raised to in rate law = 1
ii) Order is power that $[NO_2]$ is raised to in rate law = 0
iii) Order is power that $[O_2]$ is raised to in rate law = 0
b) Overall order is sum of all individual orders = 1+ 0 + 0 = 1 (first order)
c)
i) At t = 0s, Molar concentration = 2.5 mol dm^{-3}
ii) Initial rate of reaction = - gradient at t=0s

The gradient was thus measured using the straight-line segment at the time t = 0s and it was found:

-Gradient = - (- 1.5) mol $dm^{-3}\,s^{-1}$
This is equivalent to the initial rate of reaction. Therefore at this point:

Initial Rate $= k[N_2O_5]$
Therefore $k = \frac{\text{Initial Rate}}{[N_2O_5]}$
thus $k = 1.5/2.5 = 0.6\ s^{-1}$

Question 2

The formation of gaseous hydrogen iodide, HI (*g*), was monitored at a temperature of 298 K

$$H_2\,(g) + I_2\,(g) \rightarrow 2HI\,(g)$$

The following data on the rate of reaction were collected,

Initial conc $[H_2]$ / mol dm^{-3}	**Initial conc $[I_2]$ / mol dm^{-3}**	**Initial rate of reaction / mol dm^{-3} s^{-1}**
0.100	0.200	8.0×10^{-3}
0.200	0.200	16.0×10^{-3}
0.100	0.050	2.0×10^{-3}

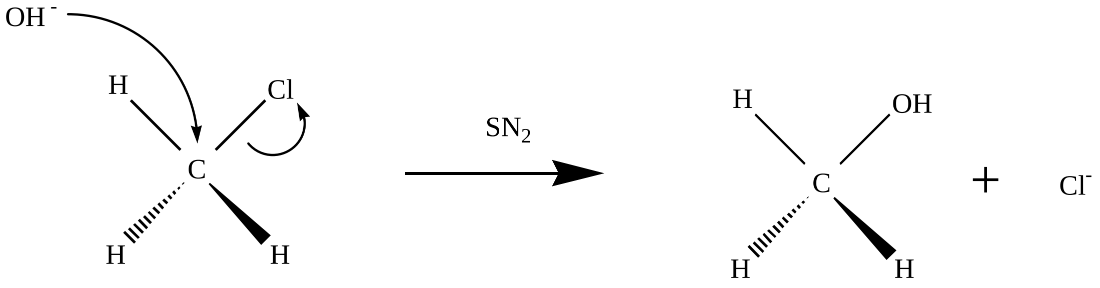
a) Derive an expression for the rate law
b) Calculate k, the rate constant for this reaction at 298 K stating clearly its units
c) Predict the initial rate of reaction at 298 K if
    Initial conc $[H_2] = 0.050$ mol dm^{-3}
    Initial conc $[I_2] = 0.050$ mol dm^{-3}

Question 3

The substitution of methyl chloride, CH_3Cl, with hydroxide ions, OH^-, obeys the following equation

$$CH_3Cl\,(aq) + OH^-\,(aq) \rightarrow CH_3OH\,(aq) + Cl^-\,(aq)$$

And has the organic mechanism:



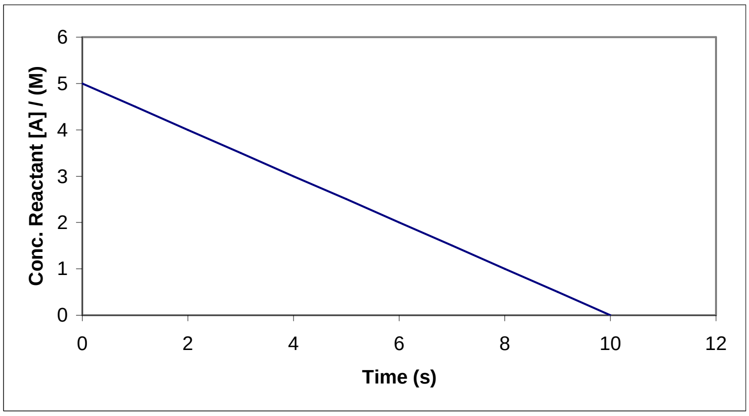
It is an SN_2 reaction with both reactants involved in the rate-determining step (RDS).

a) Suggest a rate law for this reaction
b) What is the order of reaction with respect to
  i) CH_3Cl
  ii) OH^-
c) What is the overall order of the reaction?

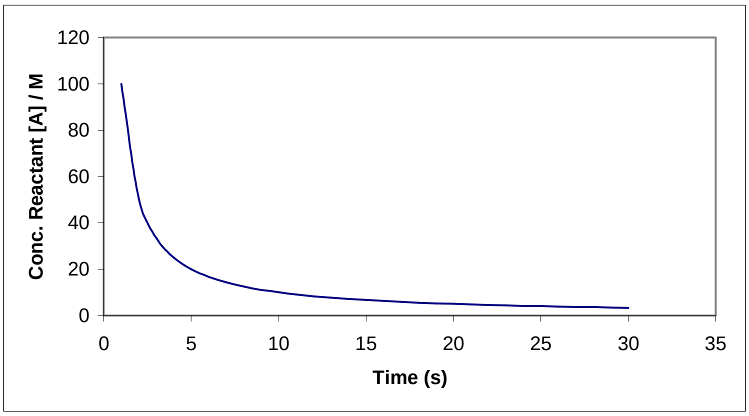
Worked Example 3

a) What graphs should be plotted to obtain straight lines for the following reaction orders?

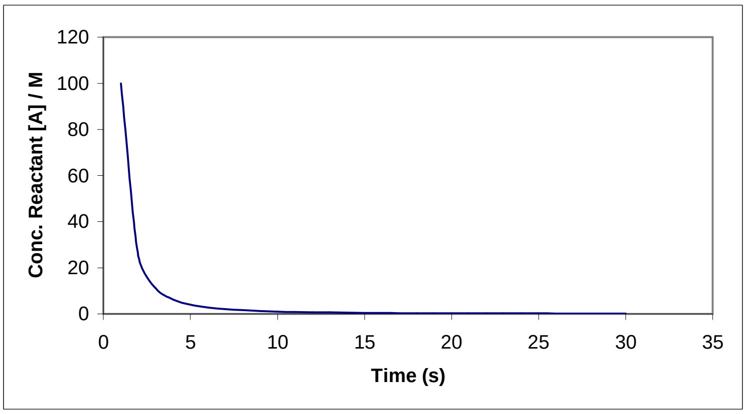
i) Zero Order – Rate = k_0



ii) First Order – Rate = $k_1[A]$



iii) Second Order – Rate = $k_2[A]^2$

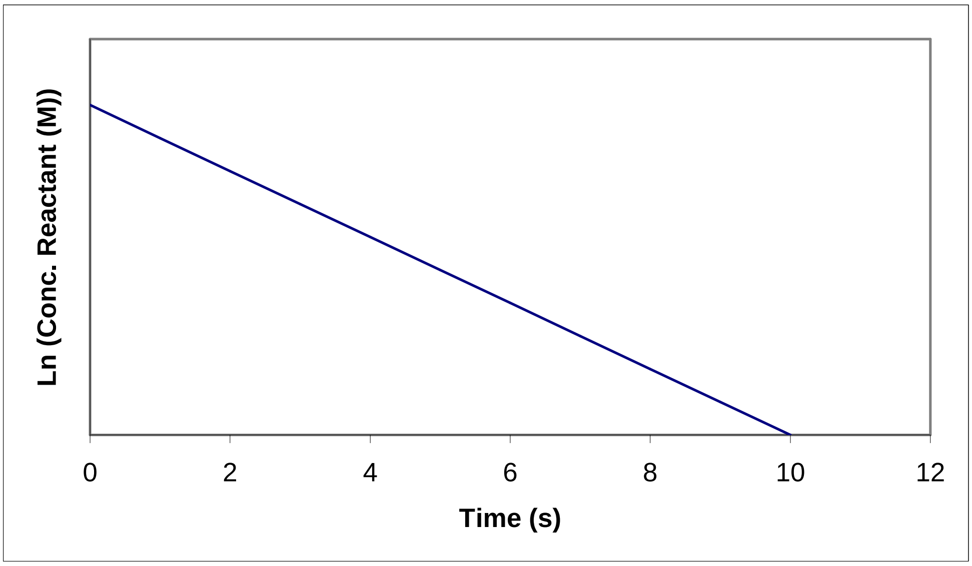


b) Given the rate equations, how could such straight-line graphs be used to calculate the rate constants and units of

i) k_0
ii) k_1
iii) k_2

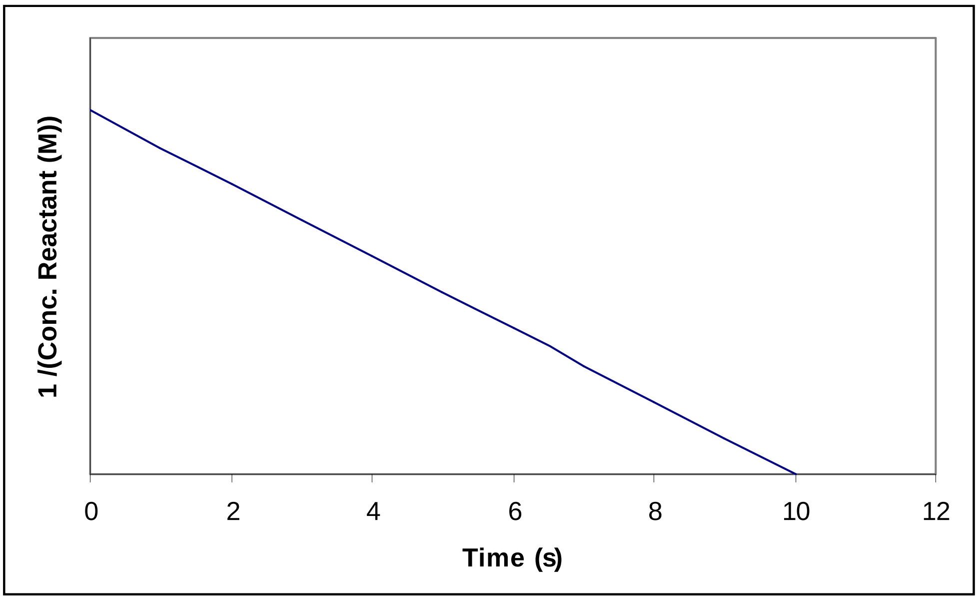
Answers

a) We use the integrated rate laws to work out what we need to plot to obtain a straight line:
i) For a zero order reaction plot [A] vs. time (as plotted in the question)



ii) For a first order reaction plot ln [A] vs. time

iii) For a second order reaction plot $\frac{1}{[A]}$ *vs. time*



b) By using the integrated rate laws and calculating the gradients of the appropriate straight line graphs,

i)

$$\frac{d[A]}{dt} = -k_0$$

$\Rightarrow [A] = -k_0t + [A]_0$ *where* $[A]_0 = [A]$ *at time = 0 s*

Which is in the form $y = mx + c$

so we plot (y vs. x) i.e. [A] vs. t and our gradient $m = -k_0$

The units are whatever gives d[A]/dt units of mol $dm^{-3}s^{-1}$ *in the rate equation. In this case,* k_0 *is the only variable on the right hand side, so must have units of mol* $dm^{-3}s^{-1}$.

ii)

$$\frac{d[A]}{dt} = -k_1[A]$$

$\Rightarrow \ln [A] = -k_1t + \ln [A]_0$

so we plot ln [A] vs. t and our gradient $m = -k_1$

Again we must let d[A]/dt have units of mol $dm^{-3}s^{-1}$*, and as [A] has units mol* dm^{-3}*, k must have units of* s^{-1}.

iii)

$$\frac{d[A]}{dt} = -k_2[A]^2$$

$$\Rightarrow \frac{1}{[A]} = k_2t + \frac{1}{[A]_0}$$

so we plot $\frac{1}{[A]}$ *vs. t and our gradient* $m = k_2$

Letting $\frac{d[A]}{dt}$ *have units of mol* $dm^{-3}s^{-1}$*, we must give k units of* $dm^3mol^{-1}s^{-1}$

Worked example 4

The decomposition of gaseous nitrogen dioxide, NO_2, was monitored at 298 K

$$NO_2\ (g) \rightarrow NO\ (g) + \tfrac{1}{2}O_2\ (g)$$

and the following data were collected:

Time/s	**$[NO_2]$ / mol dm^{-3}**
0.0	0.100
5.0	0.017
10.0	0.0090
15.0	0.0062
20.0	0.0047

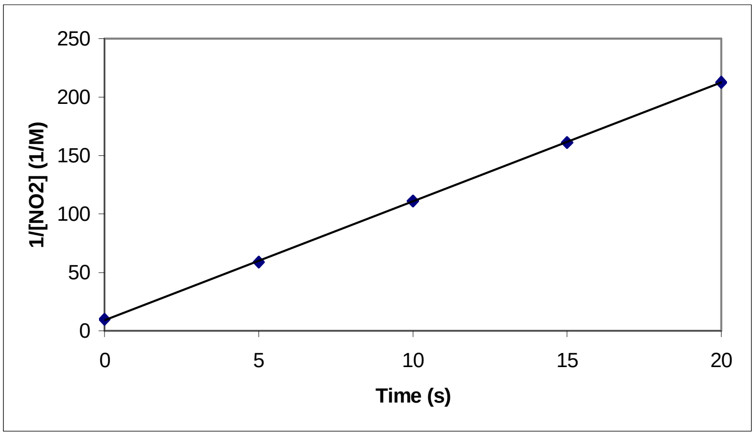
a) What is the order of the reaction with respect to nitrogen dioxide?
b) Calculate the value of the rate constant in dm^3 mol^{-1} s^{-1}.

Answers

To find the order with respect to NO_2*, we must plot a straight-line graph. We can show that the graph of* $\frac{1}{[NO_2]}$ *vs. time gives a straight line by adding another column to our table:*

Time/ s	$[NO_2]$ / mol dm^{-3}	$\frac{1}{[NO_2]}$ / dm^3 mol^{-1}
0.0	0.100	10.0
5.0	0.017	58.8
10.0	0.0090	111.1
15.0	0.0062	161.3
20.0	0.0047	212.8

And plotting the graph of $\frac{1}{[NO_2]}$ *vs. time:*



b) The straight line obtained proves the reaction is second order:

$$\frac{d[NO_2]}{dt} = -k_2[NO_2]^2$$

thus by integrating to find the integrated rate law we infer that:

$$\frac{d[NO_2]}{dt} = k_2t + \frac{1}{[NO_2]_0}$$

which has the same form as:

$$y = mx + c$$

so on our graph of 1[NO$_2$] vs. time the y-intercept is $\frac{1}{[NO_2]_0}$ *(~ 9 dm^3 mol^{-1}) and the gradient gives us our rate constant.*

From the graph, gradient m = 10.2,

Thus $k_2 = 10.2$ dm^3 mol^{-1} s^{-1}

Question 4

The dissociation of sulfuryl chloride, SO_2Cl_2, is first order with respect to SO_2Cl_2

$$SO_2Cl_2\ (g) \rightarrow SO_2\ (g) + Cl_2\ (g)$$

The reaction was performed at 298 K and the following data were obtained:

Time /s	**Conc. [SO_2Cl_2] / mol dm^{-3}**
0	1.000
2500	0.947
5000	0.895
7500	0.848
10000	0.803

a) State the rate equation for the dissociation

b) Using a graphical method, calculate the value of the rate constant, *k*, giving its units

c) Calculate the half-life for the reaction

Question 5

a) For the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

Define the variables and state their standard units

i) k

ii) A

iii) E_a

iv) R

v) T

Question 6

In the decomposition of nitrogen dioxide, NO_2, nitrous oxide and oxygen are formed as products.

$$2NO_2\ (g) \rightarrow 2NO\ (g) + O_2\ (g)$$

The reaction was performed at various temperatures and the rate constants were found to be as follows:

T/°C	***k*/ dm^3 mol^{-1} s^{-1}**
100	1.1×10^{-9}
200	1.8×10^{-8}
300	1.2×10^{-7}
400	4.4×10^{-7}

a) Rearrange the Arrhenius equation, and, by plotting a graph, find the activation energy and Arrhenius factor for the decomposition of NO_2 (Check carefully your units for the temperature)

b) Hence predict the value of k at a temperature of 500°C

Worked example 5

The reaction

$C_2H_6\ (g) \rightarrow 2CH_3^{\cdot}\ (g)$

was monitored and it was found that at 400 K, the rate constant k = 0.052 s^{-1}, and at 550 K, the rate constant k = 0.54 s^{-1}. By use of simultaneous equations, calculate the activation energy

Answers

Substituting both sets of data into the Arrhenius equation we obtain

$$0.052 = Ae^{-E_a/400R} \qquad (1)$$

and

$$0.54 = Ae^{-E_a/550R} \qquad (2)$$

Solving simultaneously by dividing (1) ÷ (2) yields

$$\frac{0.052}{0.54} = e^{E_a/550R - E_a/400R} = e^{-150E_a/220{,}000R}$$

And taking natural logarithms and rearranging gives

$$E_a = \frac{-220{,}000R}{150}\ln\left(\frac{0.052}{0.54}\right) = 28.5\,kJ\ mol^{-1}$$

Question 7

The cyclic molecule cyclopropane, C_3H_6, can undergo isomerization to propene as follows:

$C_3H_6\ (g) \rightarrow CH_3CH{=}CH_2\ (g)$

a) Assuming the reaction is first order what is the rate law for this isomerization?

b) At 500˚C, the rate constant k = $6.3\times10^{-4}\ s^{-1}$ and it is found that the Arrhenius factor A = $1.5\times10^{15}\ s^{-1}$
What is the rate constant at 650˚C?

Worked Example 6

a) Define the term *elementary step*, and describe the difference between a *unimolecular-* and *bimolecular- elementary step*.
b) Give the overall equation for the reaction mechanism:

1) H_2 (*g*) + IF (*g*) → HI (*g*) + HF (*g*) (FAST)
2) HI (*g*) + IF (*g*) → HF (*g*) + I_2 (*g*) (SLOW)

c) By consideration of the rate-determining step (RDS), suggest the rate law for the reaction.

Answers

a) An elementary step occurs in a single event. The order of such a step is given by the coefficients in the balanced equation of the step. A unimolecular elementary step has only one reactant molecule, whereas a bimolecular elementary step has two reactant molecules.

b) HI is produced in the first "initiation" step, and then destroyed in the second "propagation" step, hence HI is a "chain-carrier" and does not appear in the overall equation of the reaction:
Summing (1) and (2)

H_2 *(g) + 2IF (g) → 2HF (g) +* I_2 *(g)*

c) The slower of the two steps is the rate-determining step, i.e. the second step. This gives us the overall rate law, as we only need to take into account the RDS (and can ignore the faster step in the rate law.) The orders of the reactants in the rate law are the coefficients of the chemicals in the reaction step (in this case, one) for each reactant, giving us:

Rate = k [HI] [IF]
This is a possible rate-law based upon the mechanism proposed above. Experiments would have to be carried out to verify it.

Question 8

In aqueous solution the reaction between sodium bromide, NaBr, and hydrogen peroxide, H_2O_2, proceeds as follows

$$2\text{NaBr}\ (aq) + \text{H}_2\text{O}_2\ (aq) \rightarrow \text{Br}_2\ (aq) + 2\text{NaOH}\ (aq)$$

The proposed rate law is

$$\frac{d[\text{Br}_2]}{dt} = k[\text{NaBr}][\text{H}_2\text{O}_2]$$

a) The experiment was performed with concentrations of
$[\text{NaBr}] = 1.5 \times 10^{-3}$ mol dm^{-3}
$[\text{H}_2\text{O}_2] = 2.5 \times 10^{-3}$ mol dm^{-3}
and the rate was found to be 8.67×10^{-3} mol dm^{-3} s^{-1}.
Calculate the rate constant, *k*, giving its units.

b) What is the minimum number of elementary steps in the reaction mechanism?

c) Hence, suggest a mechanism for the reaction

Worked Example 7

In the stepwise reaction

$$A \rightarrow B \rightarrow C$$

there are the two elementary steps

1) $A \xrightarrow{k_1} B$

2) $B \xrightarrow{k_2} C$

By use of the steady state approximation on B, derive an expression for the rate of formation of C

Answer

The rate of formation of C is given by

$$\frac{d[C]}{dt} = k_2[B]$$

The rate of change of B has two terms:

$$\frac{d[B]}{dt} = +k_1[A] - k_2[B]$$

If we assume B is in the steady state as it is an intermediate then the rate of change of [B] = 0 thus

$$0 = k_1[A] - k_2[B]_{SS}$$

$[B]_{ss}$ means “steady state concentration of B”

Rearranging to find $[B]_{ss}$ we find $[B]_{SS} = \dfrac{k_1[A]}{k_2}$

We know the rate of formation of C from above so substituting in for [B] we yield

$$\frac{d[C]}{dt} = k_2 \frac{k_1[A]}{k_2} = k_1[A]$$

Which is what we would expect, as for B to be in the steady state it must react as soon as it is formed, thus the rate of reaction is entirely dependent on the first step.

Question 9

In the acid catalysed hydrolysis of an ester, E, the reaction scheme

1) $E + H_3O^+ \xrightarrow{k_1} EH^+ + H_2O$

2) $EH^+ + H_2O \xrightarrow{k_{-1}} E + H_3O^+$

3) $EH^+ + H_2O \xrightarrow{k_2}$ <rest of reaction>

where EH^+ is the protonated form of the ester, E.

By assuming EH^+ to be in the steady state show that the rate of formation of products <rest of reaction> is

$$Rate = k_{eff}[E][H_3O^+]$$

And find k_{eff} where k_{eff} is the effective rate constant (a combination of the other constants in the scheme.)

Kinetics Answers

1a) 0.1 mol s^{-1}

b) 0.1 mol s^{-1}

c) $\Delta[CH_4] / \Delta t$ = 0.1 mol s^{-1}. After 40 s 0.1 x 40 mol CH_4 used up. Therefore amount remaining = (10-4) mol = 6.00 mol

2a) From reactions (1) and (2) Rate α $[H_2]^1$

From reactions (1) and (3) Rate α $[I_2]^1$

Therefore Rate = $k[H_2][I_2]$

b) k = 0.4 $dm^3\ mol^{-1}\ s^{-1}$

c) Initial rate = 1.0×10^{-3} mol $dm^{-3}\ s^{-1}$

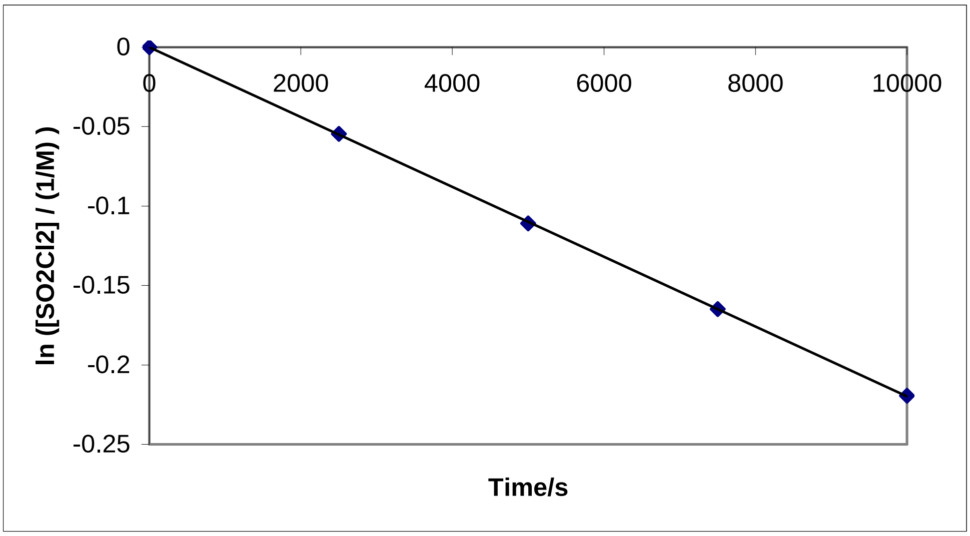
3a) Rate = k $[CH_3Cl][OH^-]$

b i) 1

ii) 1

c) 2 (Second order – hence S_N2)

4a) $d[SO_2Cl_2]/dt = -k\,[SO_2Cl_2]$



b) Graph of ln $[SO_2Cl_2]$ vs. time:

Using integrated rate law, ln $[SO_2Cl_2] = -kt + [SO_2Cl_2]_0$, and by calculation of gradient k=2.0×10^{-5} s^{-1}

c) At time t = $t_{1/2}$, one half-life, $[SO_2Cl_2] = ½\,[SO_2Cl_2]_0$ where $[SO_2Cl_2]_0$ = initial concentration

From integrated rate law: $\ln [SO_2Cl_2] = -kt + [SO_2Cl_2]_0$

Hence at $t = t_{1/2} \Rightarrow \ln\ (½ [SO_2Cl_2]_0) = -kt_{1/2} + \ln [SO_2Cl_2]_0$

$\Rightarrow t_{1/2} = (\ln 2) / k$

thus $t_{1/2} = 3.47 \times 10^4$s = 9.64 hours

5a)

i) Rate constant (units vary, $mol^{x}\, dm^{-3x}\, s^{-1}$)

ii) Pre-exponential Arrhenius factor (same as rate constant, i.e. $mol^{x}\, dm^{-3x}\, s^{-1}$)

iii) Activation energy ($kJ\ mol^{-1}$)

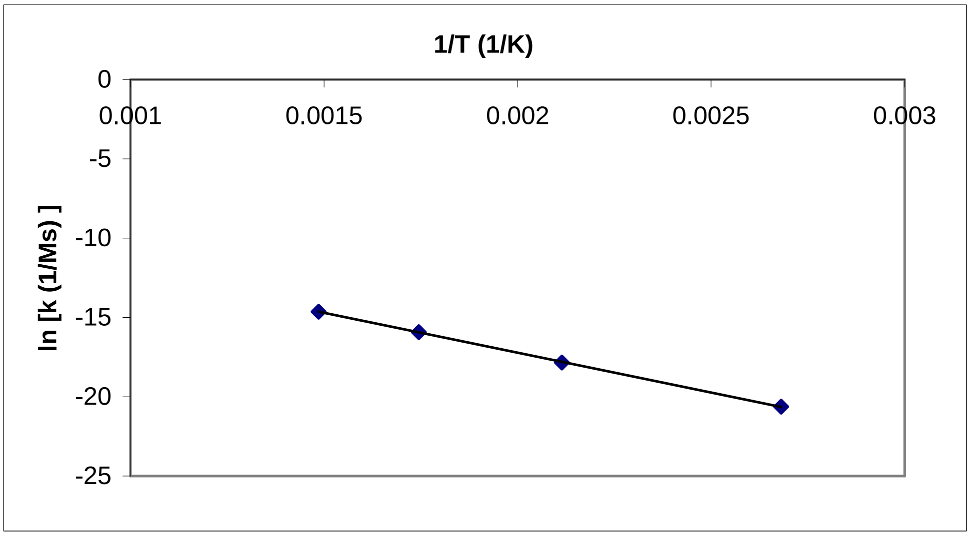
iv) Gas constant ($J\ K^{-1}\ mol^{-1}$)

v) Temperature (K)

6a) The rearranged equation is

$$\ln k = \ln A - {E_a}/{RT}$$

This equation has the form of a straight line y = mx + c so plot ln k against $\frac{1}{T}$ giving the graph. Ensure you convert temperature in ℃ to K.



From gradient

$E_a = 41.7\ kJ\ mol^{-1}$

From y-intercept

$A = 7.57 \times 10^{-4}\ dm^3\ mol^{-1}\ s^{-1}$

b) Substituting back into Arrhenius equation ⇒ $k = 1.15\times10^{-6}$ dm^3 mol^{-1} s^{-1}

7a) $-d[C_3H_6]/dt = k[C_3H_6]$

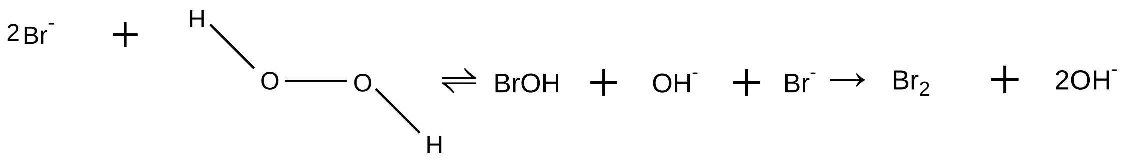
b) $k = 0.617$ s^{-1}

8a) 2.31×10^3 dm^{3}mol^{-1}s^{-1}

b) 2 steps - if the reaction were a unimolecular elementary reaction the rate law would be:

$$\frac{d\{Br_2]}{dt} = k[NaBr]^2[H_2O_2]$$

c)



9)

Overall Rate (as expressed by rate of formation of <rest of reaction> = $k_2[EH^+][H_3O^+]$

From reaction (i) $\frac{d[EH^+]}{dt} = k_1[E][H_3O^+]$

From reaction (2) $-\frac{d[EH^+]}{dt} = -k_{-1}[EH^+][H_2O]$

From reaction (3) $-\frac{d[EH^+]}{dt} = k_2[EH^+][H_2O]$

Because we are told to assume EH$^+$ is in the steady state we can say that the rate of formation of EH$^+$ is equal and opposite to the rate of consumption of EH$^+$.

Therefore: $k_1[E][H_3O]^+ = -k_{-1}[EH^+][H_2O] + k_2[EH^+][H_2O]$

Rearranging to obtain an expression for [EH$^+$]:

$$[EH^+] = \frac{k_1[E][H_3O^+]}{k_{-1}[H_2O] + k_2[H_2O]}$$

$$\text{Therefore Rate} = k_2\frac{k_1[E][H_3O^+]}{k_{-1}[H_2O] + k_2[H_2O]} \times [H_2O]$$

$$\text{Which becomes: Rate:} =[E][H_3O^+] \times \frac{k_1k_2}{k_{-1} + k_2}$$

$$k_{eff} = \frac{k_1k_2}{k_{-1}+k_2}$$

So Rate = $k_{eff}\,[\mathrm{E}][\mathrm{H_3O^+}]$

Equilibrium Reactions

Gaseous equilibria

Question 1

State which of the following statements are true about a system at equilibrium:
a) The concentration of products and reactants are the same
b) The reaction has gone to completion
c) The reaction has not gone to completion but has stopped
d) The reaction has not gone to completion and has not stopped
e) The rates of the forward and backward reactions are the same
f) The rate of the forward reaction is greater than the rate of the backward reaction at equilibrium

Question 2

Write down the expression for K_c for the following reactions and give the units (if the concentrations of the gases are measured in mol dm^{-3}):

a) $2NH_3\ (g) \rightleftharpoons N_2\ (g) + 3H_2\ (g)$
b) $2NO\ (g) + O_2\ (g) \rightleftharpoons 2NO_2\ (g)$
c) $2NO_2\ (g) \rightleftharpoons 2NO\ (g) + O_2\ (g)$
d) $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

Question 3

Calculate k_c for the following equilibrium if the concentrations at equilibrium in mol dm^{-3} are:
[NO_2] = 0.041; [CO] = 0.033; [NO] = 1.8; [CO_2] = 2.0.

$$CO\ (g) + NO_2\ (g) \rightleftharpoons NO\ (g) + CO_2\ (g)$$

Question 4

In the reaction:

$$2NO\ (g) \rightleftharpoons N_2\ (g) + O_2\ (g)$$

The initial concentration of NO (*g*) is 2.0 M, and the equilibrium concentration is “x” M.
Give an expression of k_c in terms of x.

Question 5

For the reaction:

$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

K_p is 1.78 x 10^4 at 600˚C, and 2.82x10^4 at 1000˚C. Deduce which of the following statements are true:

a) The formation of NO_2 (*g*) is favoured by a rise in temperature.
b) ΔH is negative
c) The units of K_p are atm^{-1}
d) The formation of NO_2 (*g*) is favoured by a decrease in pressure.

Question 6

For the reaction:

$2BaO_2\ (s) \rightleftharpoons 2BaO\ (s) + O_2\ (g)$

State which of the following are true for the system at equilibrium.

a) The pressure of O_2 (*g*) is proportional to the mass of BaO_2 (*s*).
b) The pressure of O_2 (*g*) is equal to the equilibrium constant, K_p.
c) If O_2 is introduced into the system, it reacts with BaO until the original pressure of O_2 at that temperature is reached.

Question 7

When N_2O_4 is kept in a flask at 1.0 atm and 298 K, it dissociates according to the following equation:

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

If its final equilibrium partial pressure is 0.82 atm what is the equilibrium partial pressure of NO_2 (*g*)?

Question 8

If K_p for the following reaction is 0.54 atm, what is the partial pressure of PCl_5, initially at 1.20 atm, when it is allowed to come to equilibrium?

$$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$$

Question 9

a) Write down the expression for K_p for the following reaction:

$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$ (A) $\Delta H^{\circ}298 = -92.4$ kJ

b) What is the relation for $K_{p,A}$ for reaction A (above) and $K_{p,B}$ for reaction B (below)?

$2NH_3 (g) \rightleftharpoons N_2 (g) + 3H_2 (g)$ (B)

c) What is the relationship between $K_{p,B}$ and $K_{p,C}$ (for the following reaction)?

$NH_3 (g) \rightleftharpoons \frac{1}{2}N_2 (g) + 1\frac{1}{2}H_2 (g)$ (C)

d) What is the relationship between K_p and K_c for reaction A?

e) Give the units of K_p for reaction A when the pressures are measured in atm.

f) Explain the effect on the value of K_p of increasing the temperature for reaction A?

Question 10

a) Describe the difference between heterogeneous and homogeneous equilibria.
b) Write down the expression for the equilibrium constant, K_p, for the thermal decomposition of ammonium carbamate, $NH_4(NH_2CO_2)$ (*s*):

$$NH_4(NH_2CO_2)\ (s) \rightleftharpoons 2NH_3\ (g) + CO_2\ (g)$$

In the above dissociation, 25.00 g of $NH_4(NH_2CO_2)$ (*s*) were placed in an evacuated 250 cm^3 flask and held at 25˚C. After some hours equilibrium was reached and 0.022 g of CO_2 were present.
c) How many moles of CO_2 and NH_3 are present at equilibrium?
d) What mass of CO_2 would have been present if 50.00 g of ammonium carbamate had been present initially?
e) Explain whether the amount of CO_2 and NH_3 is likely to increase or decrease when the temperature is raised to 50˚C.

Acid-base equilibria

Question 11

Classify aqueous solutions of the following compounds as acidic, neutral or basic:
i) KNO_3
ii) CH_3COONa
iii) CH_3CH_2OH
iv) $Al(NO_3)_3$
v) Na_2CO_3
vi) Na_3PO_4
vii) $CH_3CH_2NH_2$
viii) $(COOH)_2$

Question 12

Calculate the pH of the following:
a) 10^{-4} M HCl
b) 10^{-4} M NaOH
c) 0.01 M Propanoic acid (K_a = 1.45x10^{-5} mol dm^{-3})
d) 1 M NH_4OH (K_b = 1.7x10^{-5} mol dm^{-3})
e) A solution that is 0.015 M HF (K_a = 3.5x10^{-4} mol dm^{-3}) and 0.011 M NaF

Question 13

Give the conjugate acids of:
a) HPO_4^{2-}
b) HCO_3^-
c) OH^-

Question 14

Give the conjugate bases of:
a) NH_4^+
b) HSO_4^-
c) $H_2PO_4^-$

Question 15

The pH of 0.100 M HCOOH (*aq*) is 2.37.
a) What is the concentration of H^+ ions for this solution?
b) Write down the expression for the acid dissociation constant, K_a, for this acid.
c) What is the value of K_a for this acid?
d) What is the pH of an aqueous buffer solution containing 0.50 M NH_3 (*aq*) and 0.20 M NH_4Cl (*aq*)? [pK_a (NH_4^+) = 9.26]
e) What is the effective range of a buffer solution made from NH_3 (*aq*) and NH_4Cl (*aq*)? Explain your reasoning.

Solubility Products

Question 16

Write expressions for the solubility products of the following salts, whose solubility is represented by s mol dm^{-3}

a) Barium sulphate
b) Magnesium hydroxide
c) Lead iodate
d) Aluminium sulphide

Question 17

The solubility of magnesium carbonate at 20˚C is 1.2x10^{-3} mol dm^{-3}. Estimate K_{sp} for magnesium carbonate.

Question 18

What is the solubility of AgCl in 0.20 mol dm^{-3} NaCl? You may assume [Cl^{-}] = 0.20 mol dm^{-3}.
(K_{sp} (AgCl) = 1.6x10^{-10} mol^{2}dm^{-6})

Question 19

Determine the pH required for the precipitation of $Ni(OH)_2$ from 0.01 mol dm^{-3} $NiSO_4$ (*aq*) solution. You may assume [Ni^{2+}] = 0.01 mol dm^{-3}. [K_{sp} $Ni(OH)_2$ = 6.5 x 10^{-18} mol^{3}dm^{-9}]

Equilibrium Reactions Answers

1a) False

b) False

c) False

d) True

e) True

f) False

2a) $K_c = \dfrac{[N_2][H_2]^3}{[NH_3]^2}$ (mol^2 dm^{-6})

b) $K_c = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$ (mol^{-1} dm^3)

c) $K_c = \dfrac{[NO]^2[O_2]}{[NO_2]^2}$ (mol dm^{-3})

d) $K_c = [CO_2]$ (mol dm^{-3})

3) K_c = 2660.75

4) $K_c = x^2 / (2.0 – 2x)^2$

5a) True

b) False

c) False – units are atm

d) True – decrease in pressure causes shift to greater number of moles.

6a) False

b) True

c) True

7) 0.36 atm

8) p (PCl_5) = 0.62 atm

9a) $k_p{}^A = \dfrac{p(NH_3)^2}{p(N_2)p(H_2)^3}$

b) $K_{pB} = 1/ K_{pA}$

c) ½ as many moles therefore

$K_{pC} = (K_{pB})^{1/2}$

d) $K_p = K_c\,(RT)^{\Delta n}$ where ∆n is the change in number of moles, therefore $= K_c\,(RT)^{-1}$

e) Units are atm^{-2}

f) K_{pA} will get lower if temperature is increased, due to le Chatelier's principle.

10a) Heterogeneous equilibria have components of different physical states in them, e.g. solids and gases. Homogeneous equilibria have components of only one state present, e.g. all gases like the Haber process.

b) $K_p = p(NH_3)^2 p(CO_2)$

c) 5×10^{-4} mol CO_2

10^{-3} mol NH_3

d) The amount of ammonium carbamate does not alter the amount of CO_2 (*g*) formed, as K_p and K_c only depend upon the temperature of the system and not upon the amount of reactant used.

e) Increased amounts, the reaction is a *thermal decomposition* so is favoured by higher temperatures.

11)

i) Neutral

ii) Basic

iii) Neutral

iv) Acidic

v) Basic

vi) Basic

vii) Basic

viii) Acidic

12a) 4

b) 10

c) 3.42

d) 11.6

e) 3.32

13a) $H_2PO_4^-$

b) H_2CO_3

c) H_2O

14a) NH_3

b) SO_4^{2-}

c) HPO_4^{2-}

15a) $[H^+] = 4.27\times10^{-3}$ mol dm^{-3}

b) $K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$

c) $K_a = 1.82\times10^{-4}$ mol dm^{-3}

d) pH = 9.66

e) A buffer will not work if concentration of the base added is greater than ten times the concentration of the acid, or vice versa. Thus the equation for calculation of pH of a buffer becomes:

$pH_{min} = 9.26 + \log(1/10) = 8.26$

and

$pH_{max} = 9.26 + \log(10/1) = 10.26$

Thus pH range is:

$8.26 < pH < 10.26$

16a) $K_{sp} = [Ba^{2+}][SO_4^{2-}]$

b) $K_{sp} = [Mg^{2+}][OH^-]^2$

c) $K_{sp} = [Pb^{2+}][IO_3^-]^2$

d) $K_{sp} = [Al^{3+}]^2[S^{2-}]^3$

17) $K_{sp} = 1.44\times10^{-6}$ mol^2 dm^{-6}

18) 8.0×10^{-10} mol dm^{-3}

19) pH must be more basic than 6.41, i.e. pH > 6.41

Spectroscopy Example Questions

Question 1

State in which regions of the electromagnetic spectrum the following molecular spectra are observed:

a) Vibrational

b) rotational

Question 2

What are the two conditions required for a diatomic molecule to yield a rotational spectrum?

Question 3

A diatomic molecule acts as a rigid rotor. The total rotational energy of a diatomic molecule is given by:

$$E_{rot} = \frac{1}{2} I \omega^2$$

Define each term in the above equation and, using a diagram of a diatomic molecule describe what is meant by μ and r.

Question 4

Rotational energy levels are quantized and their values are given by the equation:

$$E_J = bJ\ (J + 1) \qquad \text{where } b = h^2/(8p^2I)$$

Define the terms b and J.

Question 5

For the following values of J calculate E_J in terms of b:

a) $J = 0$, $E_J =$

b) $J = 1$, $E_J =$

c) $J = 2$, $E_J =$

Question 6

Calculate the energy separations between the following pairs of energy levels in terms of b:

a) $J = 1$ and $J = 2$

b) $J = 2$ and $J = 3$

c) $J = 3$ and $J = 4$

Question 7

a) Using the information calculated above predict what happens to the separation of the rotational energy levels as the quantum number increases.

b) Which molecule will have the larger separation of rotational energy levels, ICl or HCl?

Question 8

a) The rotational constant, b, for an NO molecule has the value 1.695 cm^{-1}. Using this value, calculate the moment of inertia, I, of NO.

b) Calculate the reduced mass, in kg, of NO.

c) Calculate the bond length of NO.

d) Compare this value with literature values for N_2 and O_2 and comment on your answer.

Question 9

Which of the following molecules will give rise to an observable gaseous infrared spectrum at room temperature?

Cl_2 HCl CO H_2 CH_3CH_3 H_2O

Question 10

The stretching frequency for a bond depends upon the force constant, *f*, for the bond and the reduced mass of the atoms comprising the bond according to the formula:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}}$$

If a typical C=O stretch is 1750 cm^{-1} would you expect the v(C-O) stretch to be higher or lower frequency?

Would you expect the v(S=O) to be at a higher or lower frequency than the v(C=O)?

Spectroscopy Example Questions – Model Answers

Question 1

State in which regions of the electromagnetic spectrum the following molecular spectra are observed:

a) vibrational **Infrared region (10^{11} – 10^{14} v^{-1})**

b) rotational **Microwave region (10^{10} – 10^{11} v^{-1})**

Question 2

What are the two conditions required for a diatomic molecule to yield a rotational spectrum?

1) the molecule must have a dipole moment

2) the quantum number can only change by ±1

Question 3

A diatomic molecule acts as a rigid rotor. The total rotational energy of a diatomic molecule is given by:

$$E_{rot} = \tfrac{1}{2} I \omega^2$$

Define each term in the above equation and, using a diagram of a diatomic molecule describe what is meant by *μ* and r.

E_{rot} is the rotational energy of the molecule

I is the moment of inertia of the molecule and may be calculated as:

$$I = \sum_i m_i r_i^2 \quad \text{or} \quad I = \mu \bullet r^2$$

***μ* is the “reduced mass” $\left[\mu = \dfrac{m_1 m_2}{m_1 + m_2}\right]$ where m_1 and m_2 are the masses of the two atoms in a diatomic molecule and *r* is the bond length.**

ω is the angular velocity.

Question 4

Rotational energy levels are quantized and their values are given by the equation:

$$E_J = bJ\,(J + 1) \qquad \text{where } b = h^2/(8p^2I)$$

Define the terms b and J.

b is the rotational constant for the molecule and can be defined as:

$$\mathbf{b} = \frac{h}{8\pi^2 Ic}$$

J is the quantum number and can have the values 0, 1, 2, 3, 4, etc.

Question 5

For the following values of J calculate E_J in terms of b:

a) J = 0, E_J = **0**

b) J = 1, E_J = **2b**

c) J = 2, E_J = **6b**

Question 6

Calculate the energy separations between the following pairs of energy levels in terms of b:

a) J = 1 and J = 2 **= (6b – 2b) = 4b**

b) J = 2 and J = 3 **= (12b – 6b) = 6b**

c) J = 3 and J = 4 **= (20b – 12b) = 8b**

Question 7

a) Using the information calculated above predict what happens to the separation of the rotational energy levels as the quantum number increases.

It increases linearly by a factor of 2b for each additional quantum number, J, increased.

b) Which molecule will have the larger separation of rotational energy levels, ICl or HCl?

Calculate rotational constant, b, for each molecule.

Question 8

a) The rotational constant, b, for an NO molecule has the value 1.695 cm^{-1}. Using this value, calculate the moment of inertia, I, of NO.

$$I = \frac{h}{8\pi^2 bc} = 16.512 \times 10^{-47}\ \text{kg m}^2$$

b) Calculate the reduced mass, in kg, of NO.

$$\left[\mu = \frac{m_1 m_2}{m_1 + m_2}\right] \times 1.6605 \times 10^{-27} = 1.24 \times 10^{-26}\ \text{Kg}$$

c) Calculate the bond length of NO.

$$\text{I} = \mu \bullet r^2 \qquad r = \sqrt{\frac{I}{\mu}}$$

$$= \sqrt{\frac{16.512 \times 10^{-47}}{1.24 \times 10^{-26}}} = 1.15 \times 10^{-10}\ \text{m}$$

$$= 115\ \text{pm}$$

d) Compare this value with literature values for N_2 and O_2 and comment on your answer.

N_2 = 111 pm

O_2 = 121 pm

NO = intermediate value.

Question 9

Which of the following molecules will give rise to an observable gaseous infrared spectrum at room temperature?

Cl_2	HCl	CO	H_2	KBr	H_2O
No	**Yes**	**Yes**	**No**	**Yes**	**Yes**

Question 10

The stretching frequency for a bond depends upon the force constant, *f*, for the bond and the reduced mass of the atoms comprising the bond according to the formula:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}}$$

If a typical C=O stretch is 1750 cm^{-1} would you expect the v(C-O) stretch to be higher or lower frequency?

Increase in force constant = Increase in stretching frequency

Would you expect the v(S=O) to be at a higher or lower frequency than the v(C=O)?

Change in atomic weight = change in reduced mass.

v(S=O) = higher reduced mass so will reduce the frequency.