RIO TINTO AUSTRALIAN SCIENCE OLYMPIADS

AUSTRALIAN SCIENCE OLYMPIADS

QUALIFYING EXAMINATION

CHEMISTRY 1997

GENERAL INSTRUCTIONS

(1) This paper is in **two** sections and you must answer each section according to the instructions.
ie. Section A: Answer **ALL** questions
Section B: Question 16 is **compulsory**
Answer **any two** of Questions 17, 18 or 19

(2) All answers must be written in the space provided in the answer book.

(3) **Use blue or black pen to write your answers**, pencil is not acceptable.

(4) Rough working must be done only in the indicated areas of the answer book.

(5) You are not permitted to refer to books, periodic tables or written notes and the only permitted aid is a non-programmable electronic calculator.

(6) You are permitted **15 minutes** to read the paper and supply the requested information on the cover of the answer book, followed by **120 minutes** to work the questions.

(7) Relevant data that may be required for a question will be found on page 2.

DATA

Avogadro constant (N)	6.02×10^{23} mol^{-1}
1 faraday	96,486 coulombs
1 coulomb	1 amp sec
Universal gas constant (R)	8.314 J K^{-1} mol^{-1} 8.206×10^{-2} L atm K^{-1} mol^{-1}
Planck's constant (h)	6.626×10^{-34} J s
Standard temperature and pressure (STP)	273 K and 101.3 kPa 0˚C and 101.3 kPa 0˚C and 1 atm
Molar volume of ideal gas at STP	22.4 L
Velocity of light (c)	2.998×10^{8} ms^{-1}

ATOMIC NUMBERS & RELATIVE ATOMIC MASSES*

1	H	1.008	23	V	50.94	45	Rh	102.9	67	Ho	164.9	89	Ac	(227)
2	He	4.003	24	Cr	52.00	46	Pd	106.4	68	Er	167.3	90	Th	232.0
3	Li	6.941	25	Mn	54.94	47	Ag	107.9	69	Tm	168.9	91	Pa	(231)
4	Be	9.012	26	Fe	55.85	48	Cd	112.4	70	Yb	173.0	92	U	238.0
5	B	10.81	27	Co	58.93	49	In	114.8	71	Lu	175.0	93	Np	(237)
6	C	12.01	28	Ni	58.69	50	Sn	118.7	72	Hf	178.5	94	Pu	(244)
7	N	14.01	29	Cu	63.55	51	Sb	121.8	73	Ta	180.9	95	Am	(243)
8	O	16.00	30	Zn	65.38	52	Te	127.6	74	W	183.9	96	Cm	(247)
9	F	19.00	31	Ga	69.72	53	I	126.9	75	Re	186.2	97	Bk	(247)
10	Ne	20.18	32	Ge	72.59	54	Xe	131.3	76	Os	190.2	98	Cf	(251)
11	Na	22.99	33	As	74.92	55	Cs	132.9	77	Ir	192.2	99	Es	(252)
12	Mg	24.31	34	Se	78.96	56	Ba	137.3	78	Pt	195.1	100	Fm	(257)
13	Al	26.98	35	Br	79.90	57	La	138.9	79	Au	197.0	101	Md	(258)
14	Si	28.09	36	Kr	83.80	58	Ce	140.1	80	Hg	200.6	102	No	(259)
15	P	30.97	37	Rb	85.47	59	Pr	140.9	81	Tl	204.4	103	Lw	(260)
16	S	32.06	38	Sr	87.62	60	Nd	144.2	82	Pb	207.2	104	Db	
17	Cl	35.45	39	Y	88.91	61	Pm	(145)	83	Bi	209.0	105	Jt	
18	Ar	39.95	40	Zr	91.22	62	Sm	150.4	84	Po	(209)	106	Rf	
19	K	39.10	41	Nb	92.91	63	Eu	152.0	85	At	(210)	107	Bh	
20	Ca	40.08	42	Mo	95.94	64	Gd	157.3	86	Rn	(222)	108	Hn	
21	Sc	44.96	43	Tc	(98)†	65	Tb	158.9	87	Fr	(223)	109	Mt	
22	Ti	47.88	44	Ru	101.1	66	Dy	162.5	88	Ra	226.0			

* The relative values given here are to four significant figures.

† A value given in parentheses denotes the mass of the longest-lived isotope.

SECTION A

It is intended that candidates devote not more than **30 minutes to this section**. Answer **ALL** fifteen (15) questions in this section. Only one choice is allowed per question and this should be made by clearly crossing the chosen answer box in **the answer book**. If you make a mistake **correct it clearly** so that the examiners can read your answer.

Q1 What is the formula of a substance with mass percentages of 35.97% for S, 62.92% for O and 1.13% for H?

- **A** H_2SO_3
- **B** H_2SO_4
- **C** $H_2S_2O_4$
- **D** $H_2S_2O_7$
- **E** $H_2S_2O_8$

Q2 Which species can be described as having sp^3d hybridisation?

1 PCl_5 2 SF_4 3 I_3^-

- **A** 1 only
- **B** 2 only
- **C** 1 and 2 only
- **D** 1, 2 and 3
- **E** 1 and 3 only

Q3 Carbon monoxide reacts with water vapour in a balanced equation:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad \Delta H° = -41.13 \text{ kJ}$$

Under what conditions could we get a maximum yield of products?

- **A** at low temperature
- **B** at high temperature
- **C** at low temperature and low pressure
- **D** at high temperature and high pressure
- **E** at low temperature and high pressure

Q4 Which combinations of equal volumes of solution will result in buffer solutions?

1 0.1 M HCl and 0.1 M NH_3

2 0.1 M HNO_2 and 0.05 M NaOH

3 0.05 M HNO_2 and 0.05 M NH_3

- **A** 1 only
- **B** 2 only
- **C** 1 and 2 only
- **D** 1 and 3 only
- **E** 2 and 3 only

Q5 Which represents an acid-base reaction according to the Lewis definition but **not** the Brønsted-Lowry definition?

A $MgCl_2(s) \rightleftharpoons Mg^{2+}(aq) + 2Cl^{-}(aq)$

B $CN^{-}(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^{-}(aq)$

C $NH_3(g) + HBr(g) \rightleftharpoons NH_4Br(s)$

D $Fe(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(H_2O)_5OH]^{2+}(aq) + H_3O^{+}(aq)$

E $HF(aq) + OH^{-}(aq) \longrightarrow H_2O(l) + F^{-}(aq)$

Q6 For which element are the oxidation states given actually observed ***and*** the underlined state the most stable?

A Ca (Z = 20) +1, <u>+2</u>

B Cr (Z = 24) <u>+2</u>, +3, +6

C In (Z = 49) <u>+3</u>, +5

D Cu (Z = 29) <u>+1</u>, +2

E Pb (Z = 82) <u>+2</u>, +4

Q7 Which of the following molecules will be linear?

A H_2Se

B PH_3

C H_2O

D O_3

E HCN

Q8 The electrochemical series uses this reaction as a standard.

$$2H^{+} + 2e^{-} \longrightarrow H_2$$

In order for this half cell to have a potential of 0.00 V, all of the following are required ***except***

A a solution with $[H^{+}]$ concentration = 1.0 M

B hydrogen gas at a pressure of 1.0 atm

C an external source of electrons

D an electrode made of an inert metal such as platinum

E an atmospheric temperature of 25°C

Q9 Calculate the wavelength of light required to break the bond between two chlorine atoms in a chlorine molecule. The Cl—Cl bond energy is 243 kJ mol^{-1}

A 9.34×10^{-34} m

B 8.18×10^{-31} m

C 6.26×10^{-21} m

D 4.93×10^{-7} m

E 4.11×10^{-6} m

Q10 A 0.100 M solution of acetic acid is titrated with a 0.100 M solution of NaOH. What is the pH when 50% of the acid has been neutralised? K_a for acetic acid is 1.8×10^{-5}

A 2.38

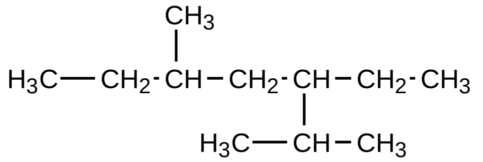
B 4.74

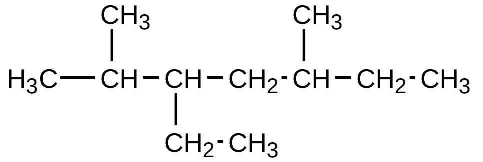
C 5.70

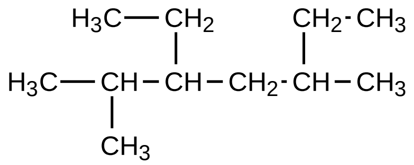
D 7.00

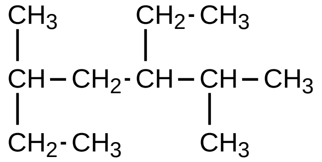
E 10.76

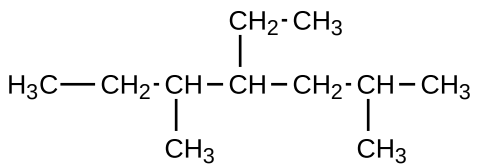
Q11 Most of the five hydrocarbons below are structurally identical.

1 

2 

3 

4 

5 

Identify the different structure.

A 1

B 2

C 3

D 4

E 5

Q12 At 0°C the ionic product constant of water, K_w, is 1.2×10^{-15}. The pH of pure water at this temperature is

A 6.88

B 7.00

C 7.46

D 7.56

E 7.68

Q13 What is the density (in g mL^{-1}) of a 3.60 M aqueous sulfuric acid solution that is 29.0% H_2SO_4 by mass?

A 1.22

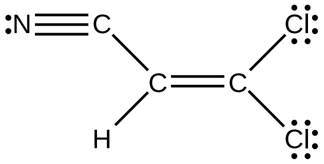
B 1.45

C 1.64

D 1.88

E 1.92

Q14 How many sigma bonds and how many pi bonds are represented in the following structure?



A 5 sigma and 4 pi

B 6 sigma and 3 pi

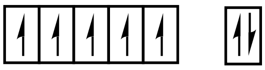
C 7 sigma and 2 pi

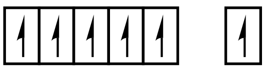
D 8 sigma and 1 pi

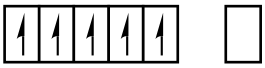
E 9 sigma and 0 pi

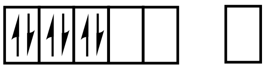
Q15 The atomic number of iron is 26. The electronic structure of the Fe(III) ion may be represented as

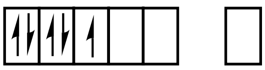
3*d* 4*s*

A Ar 

B Ar 

C Ar 

D Ar 

E Ar 

SECTION B

Candidates are advised that the correct use of significant figures will be taken into consideration when marking answers to these problems. Candidates are also advised that steps to the solution of problems must be clearly explained. Marks will be deducted for untidy and poorly explained answers.
Question 16 is compulsory. You have a choice of answering any two questions of the remaining three questions.

Compulsory question

Candidates should note that for calculations they are required to give answers both as expressions and as computed results. Failure to provide either of these will result in marks being deducted.

Q16 Chrome-vanadium steel is a valuable alloy for making high speed machine tools. In the modern laboratory it is analysed spectroscopically but the classical volumetric analysis required the subtle interplay of numerous redox reactions. Pit your skills against those of the classic analyst.

A sample of chrome-vanadium steel weighing 2.00 g was dissolved in a mixture of sulfuric and phosphoric acids. Oxidants were then added to raise the oxidation state of iron to Fe^{3+} the chromium to $Cr_2O_7^{2-}$ the vanadium to VO_3^- and the manganese to MnO_4^-. In short all these elements were in their highest oxidation state. The solution was then treated with a few drops of HCl and the resulting solution still containing Fe^{3+}, $Cr_2O_7^{2-}$ and VO_3^- then treated with 25.00 mL of 0.1010 M $FeSO_4$. This resulted in the reduction of $Cr_2O_7^{2-}$ and VO_3^- to Cr^{3+} and VO^{2+} respectively. The Fe^{2+} and VO^{2+} in this solution was then titrated with 0.02236 M $KMnO_4$ and required 12.60 mL to reach the equivalence point.

A small volume of Fe^{2+} was then added to again reduce the VO_3^- produced by the $KMnO_4$ back to VO^{2+} and this then titrated directly with 0.02236 M $KMnO_4$ a process requiring 0.86 mL to reach the equivalence point.

(a) Why was it necessary to add the HCl before commencing the titration?

(b) Write balanced half equations for

(i) The reduction of $Cr_2O_7^{2-}$.

(ii) The oxidation of Fe^{2+}.

(iii) The reduction of VO_3^-.

(iv) The reduction of MnO_4^-.

and hence

(c) Write balanced ionic equations for the following reactions

(i) $Cr_2O_7^{2-}$ with Fe^{2+}

(ii) VO_3^- with Fe^{2+}

(iii) MnO_4^- with Fe^{2+}

(d) Calculate the following quantities

(i) The moles of Fe^{2+} in the 25.00 mL sample of standard $FeSO_4$ solution.

(ii) The moles of Fe^{2+} titrated with 12.60 mL of standard $KMnO_4$.

(iii) The moles of Fe^{2+} consumed by the $Cr_2O_7^{2-}$.

(iv) The moles of chromium in the steel sample and hence the % chromium present in the sample.

(e) Calculate the % of vanadium in the steel sample.

Q17 Compound **A** is a white crystalline, ionic compound that is widely used as a fertiliser and as an explosive in mining and quarrying operations. It decomposes explosively above *ca* 300°C to give two colourless and odourless diatomic gases **B** and **C**, and H_2O. At lower temperatures (*ca* 250°C) **A** decomposes to give a triatomic gas **D** and H_2O. **D** is used as a mild anaesthetic and a propellant for whipped cream (due to its high solubility in fat). Like **A**, **D** is thermodynamically unstable and decomposes on heating to **B** and **C**.

Compound **A** is prepared commercially by reacting gaseous **E** with **F**. **E** has a distinctive, irritating, pungent odour and can be produced by the action of dilute aqueous NaOH on **A**, upon heating. (**E** is not the sole product of the reaction). Commercially, **E** is prepared by reacting **B** and H_2 in the presence of an iron oxide catalyst at high temperature (*ca* 400 °C) and high pressure (*ca* 250 atm).

F is a strong acid and a strong oxidising agent. It is prepared commercially via a three step process:

- Reaction of **E** with **C** at *ca* 850°C, in the presence of a catalyst, produces a colourless, diatomic gas **G** and H_2O. (Reaction of atomic oxygen with **D** also produces **G**).
- Further reaction of **G** with **C** produces a brown, triatomic gas **H** which exists in equilibrium with colourless **I**. **I** is isoelectronic with $C_2O_4^{2-}$ the oxalate ion.
- **H** disproportionates in H_2O to produce **F** and **G** with the latter being recycled.

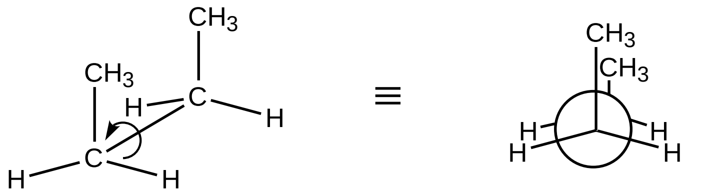
(a) (i) Identify compounds **A**-**I** and .

(ii) Write a balanced equation for each of the reactions.

(b) Draw Lewis structures for **D**, **E**, **F**, **H** and **I**.

(c) Why is the reaction of **H** with H_2O termed a disproportionation reaction?

Q18 Shape or molecular geometry is an important feature of the reactivity of organic molecules. For example the molecule of butane (C_4H_{10}) can be examined for different energy states, called conformers, by recalling that the two ends of the molecule may rotate around the central carbon-carbon bond, like propellers. This is referred to as "free rotation". The highest energy conformer of butane is one in which repulsions between groups is at a maximum and this is shown as a so called "saw-horse" diagram and Haworth projection below.



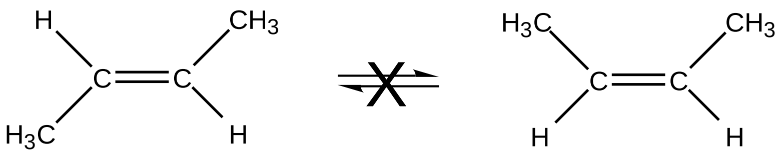
Saw-horse diagram Haworth projection

Recalling that so called "steric repulsions" are a result of repulsions caused by bonding and non-bonding electrons around atoms, and that large groups such as CH_3 are closer through space than hydrogens.

(a) (i) Use the Haworth projection to show the minimum energy conformer of butane.

(ii) Likewise draw a conformer which is energetically between the one shown in the question above and your answer to (i).

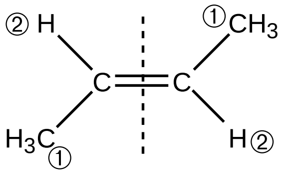
Double bonds unlike single bonds are rigid and the two ends are no longer able to undergo free rotation. As a consequence the molecule of but-2-ene can exist as two non interconverting isomers.



(*E*)-but-2-ene (*Z*)-but-2-ene

These are designated *E* and *Z* isomers respectively. Assigning the symbol (called a stereodesignator) *E* or *Z* is easy once you understand the rules. Simply these say you look at each half of the molecule in turn and assign priorities to the groups attached to the double bond according to the atomic number of the atom attached directly to the double bond.

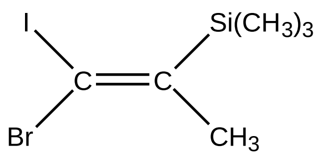
ie.



C (atomic number = 6) > H (atomic number =1)

If the two priority groups designated ① are on opposite sides of the double bond the (*E*) designator is applied and if they are on the same side of the double bond the (*Z*) designator is applied.

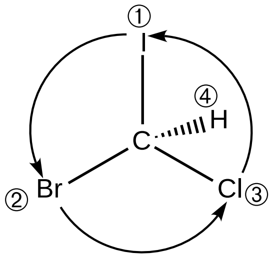
(b) Assign the correct stereodesignator to the following molecule.



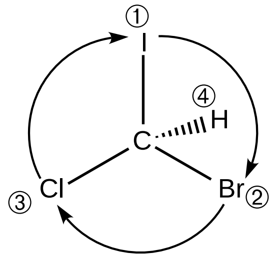
(Q18 is continued on the next page)

(Q18 continued)

Saturated carbons which contain four different groups exist as mirror images which cannot be superimposed upon each other. These are called enantiomers, and are distinct compounds which cannot interconvert. They too have special stereodesignators (*R* and *S*).



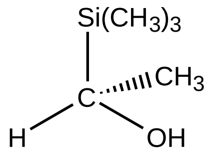
(*S*)-bromochloroiodomethane



(*R*)-bromochloroiodomethane

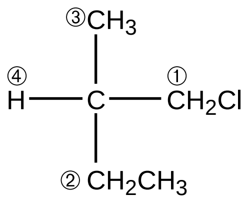
Again this utilises priorities based on atomic number (see above). The lowest priority group, ④, is placed directly away from the eye. The other three groups must then increase in priority in an anticlockwise sense (*S*) or in a clockwise sense (*R*).

(c) Assign the correct stereodesignators to the molecule shown below.



Simple as these rules are they do not address all questions. A decision on priorities can **not** always be made by looking at atoms bonded directly to the central carbon, and if this occurs one simply keeps moving outward until a decision can be made using the atomic number rule.

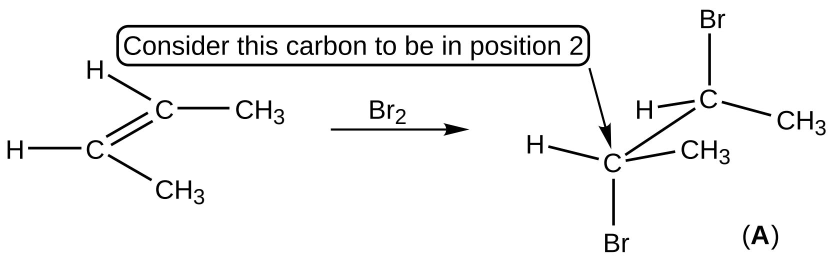
ie.



Using this information you can now attempt the next question.

The addition of bromine to a double bond occurs in such a way that bromine adds to different faces of the double bond.

ie.



(**A**)

(d) (i) The name, ignoring stereodesignators, for the product (**A**) of the reaction immediately above is 2,3-dibromobutane. Each of the carbons at position 2 and 3 should be assigned either *R* or *S*.

Complete the name for the reaction product (**A**),

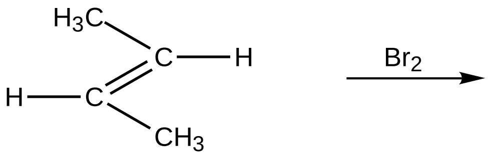
(2...... ,3 ....)-2,3-dibromobutane

by adding (in your answer book) *R* or *S* as appropriate in the spaces after the numbers 2 and 3.

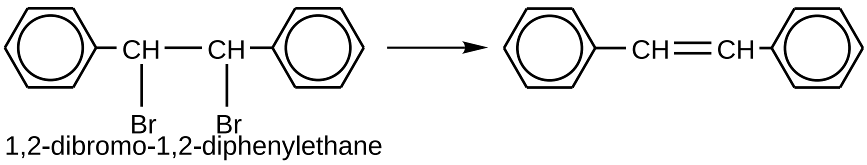
(Q18 is continued on the next page)

(Q18 continued)

(ii) Using the saw-horse form draw a diagram, in your answer book, to complete the following reaction.



(e) Now try to put all these ideas together. The following reaction



1,2-dibromo-1,2-diphenylethane

has been extensively studied. It is known that the loss or elimination of bromine occurs from the conformer in which the bromines are as far removed as possible from one another. For the (1*S*, 2*S*) isomer of 1,2-dibromo-1,2-diphenylethane,

(i) Draw in saw-horse form the conformer from which the elimination of Br_2 occurs.

and then

(ii) Predict which isomer, *E* or *Z* of the corresponding alkene will be formed.

(iii) Finally decide if the outcome would be the same if you started with a one to one mixture of the enantiomers, ie the (1*S*, 2*S*) and (1*R*, 2*R*) enantiomers, of 1,2-dibromo-1,2-diphenylethane, and briefly explain your reasoning.

Q19 Consider the molecule cyclohexane, Figure 1(a). In reality it is not a flat ring, but can exist in two *conformations*, the “chair” and “boat”, Figs 1(b) and 1(c) respectively. The reaction

$$\text{boat} \longrightarrow \text{chair} \qquad (\mathbf{1})$$

is exothermic in the forward direction and has an activation energy, so we can represent the reaction with a graph like Figure 2.

For clarity only the carbon atoms are shown in the following three diagrams the hydrogen atoms are not shown.

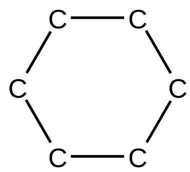


Figure 1(a): Cyclohexane

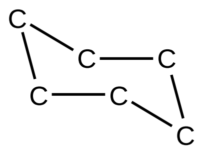


Figure 1(b): Chair
The 4 central atoms form a plane, the leftmost is above this plane, the rightmost below

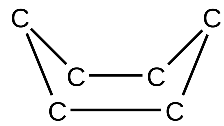


Figure 1(c): Boat
Again the 4 central atoms form a plane, the outer ones are both above this plane

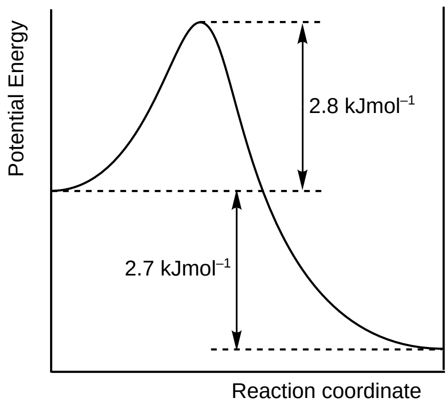


Figure 2:
The energy profile for the inter conversion of boat and chair

Now consider a container of cyclohexane vapour. If we take a sufficiently large collection of cyclohexane molecules (maybe 100 or 1000), and represent them as marbles rolling about on the graph in Figure 2 then we have quite a good simulation of the system. The kinetic theory of gasses - the work of Messrs Maxwell and Boltzman, tells us that when a marble hits the edge of the graph, it will bounce off with an energy randomly distributed in a range that depends upon the temperature of the system. In a nutshell, this says that the probability of a marble getting over the hill after bouncing off a wall is given by

$$P = e^{-\left(\frac{\Delta E}{k_b T}\right)} \qquad (\mathbf{2})$$

where k_b is Boltzman’s constant (1.38×10^{-23} JK^{-1}), ΔE is the vertical distance to the top of the hill (in Joules per molecule) and T is the temperature inside the container (in Kelvin).

The equilibrium constant for reaction **1** is

$$K = \frac{\text{number of chair molecules at equilibrium}}{\text{number of boat molecules at equilibrium}} \qquad (\mathbf{3})$$

(Q19 is continued on the next page)

(Q19 continued)

The value of this constant can be obtained from the simulated system outlined above by the following iterative process:

•1 Put all the marbles on one side of the hill.

•2 Let every marble bounce off the walls **once** (Assume that these magic marbles never bump into each other), and work out where all the marbles are now.

•3 Repeat (•2) until the number of marbles on each side no longer changes. (Note that because there are an integer number of marbles, you may find that one marble hops back and forth. This is just numerical error and you can stop if it happens).

For example, if the forward reaction had a hill 1 kJmol^{-1}, and the reverse reaction a hill of 2 kJmol^{-1}, and the temperature is 300 K then the calculation would proceed as follows.

•1 Start with 100 marbles (molecules) of reactant.

•2 The number of marbles that will convert to product is

$$100 \times e^{-\left(\frac{1000 / 6.02 \times 10^{23}}{1.38 \times 10^{-23} \times 300}\right)} = 67$$

•3 Thus, when we begin again, we have 33 "reactant marbles" and 67 "product marbles". Repeating the calculation gives

$$33 \times e^{-\left(\frac{1000 / 6.02 \times 10^{23}}{1.38 \times 10^{-23} \times 300}\right)} = 22$$ reactant marbles convert to product and

$$67 \times e^{-\left(\frac{2000 / 6.02 \times 10^{23}}{1.38 \times 10^{-23} \times 300}\right)} = 30$$ product marbles convert back to reactant

and we now have 33 - 22 + 30 = 41 "reactant marbles" and 67 - 30 + 22 = 59 "product marbles". The calculation would be repeated until the number of marbles in each position stopped changing.

(a) Use the iterative procedure above to evaluate the equilibrium constant, K, at 25°C and 200°C. For both temperatures record the results, in the answer book, for each calculation that you had to do in step •2 above.

(b) Explain the difference in K values at the two temperatures. What value do you think K will approach at very high temperatures? Why?

(c) (i) To what event in the real system does "bouncing off the walls" correspond?

(ii) What determines, in the real system, the average time between each bouncing?

(iii) On the basis of your previous answers, explain the effect of temperature on reaction rate.

(iv) What would be the effect on the rate at which equilibrium was reached if the experiment was repeated with high pressure helium gas added to the container?

(v) Given that the kinetic energy (E) of a molecule can be calculated by

$$E = \tfrac{1}{2}\left(mv^2\right)$$ (**4**)

(where m is the mass of the molecule and v its velocity), what difference, if any, would there be if argon were used in place of helium in part (iv)?

In reality, the profile of the energy hill cannot usually be defined in terms of one parameter (the *reaction coordinate*) alone. For instance, there is often a geometric factor that relates to the relative orientations of two molecules when they collide. The resulting *potential surface* is shown in Figure 3. The marbles used for illustration above begin in a long line with fixed reaction coordinate (ie they are all reactant molecules) but with different geometric factors (orientations in space).

(Q19 is continued on the next page)

(d) How would the width of the saddle affect the rate of reaction? What about the equilibrium constant?

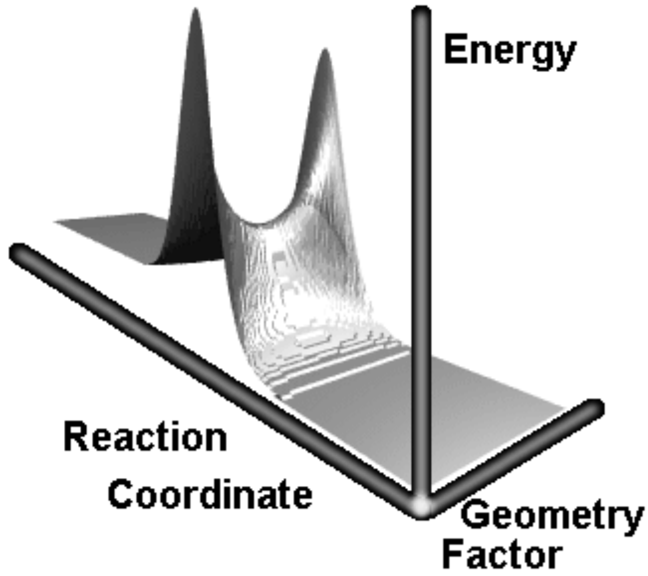


Figure 3: Generalised Potential Surface

(e) Consider the reactions in Figure 4. In each case, the OH^- ion must approach the carbon atom through the "gap" opposite the iodine atom. What does the geometric factor correspond to in this case?

(f) Which reaction would you expect to proceed to equilibrium faster? Why?

Figure 4: Substitution of a) Iodomethane and b) 2-iodo-2-methylpropane