

Calculations in Advanced Physical Chemistry

Third Edition

**P. J. F. Griffiths and
J. D. R. Thomas**

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Preface to Third Edition

This book has already helped several generations of students to acquire an enhanced perception of physical chemistry through problem solving during their university or equivalent courses. Since pocket calculators have become generally available, previously tedious arithmetical chores can now be completed in a very short time so that present day students can obtain very quickly a wider experience of problem solving than was previously possible. Problem solving ability may be measured by examining authorities by means of numerical multiple choice questions. Such questions are in wide use by universities throughout the world, and particularly so in North America. These questions can be answered more efficiently if the student has acquired the kind of understanding that may be obtained through dedicated practice via the wide variety of additional problems following each chapter of worked examples in this book.

Correspondence received shows that this book is used in many parts of the world (the second edition has also been translated into Hungarian), so that the authors have taken the opportunity in this third edition to include questions from a greater range of universities and examining bodies. The following are thanked for their goodwill in sending questions, for their kind permission to use the questions, and in some instances for allowing them to be adapted to a more conventional form, especially when they were of the multiple choice variety:

University of Toronto, Canada

Professor M. Thompson, University of Toronto,

Professor Henry Freiser and Professor W. R. Salzman, University of Arizona, Tucson, USA;

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American Chemical Society (ACS), USA;

University of Oxford, England, for questions for Final Examination papers set by the Honour School of Natural Science, Oxford: General Physical Chemistry II, reprinted by permission of Oxford University Press.

The authors also reiterate their thanks to the examining authorities named in the preface to the first edition. Among these authorities was the Royal Institute of Chemistry (R.I.C.), now unified with the Chemical Society into the Royal Society of Chemistry (R.S.C.). Hence the questions of R.I.C. origin are now attributed to R.S.C.

In addition to the larger number and wider range of questions now included, nomenclature has been modernized, and Chapter 10 (Spectra) has been substantially extended to cover statistical thermodynamics.

Finally the authors acknowledge a debt of gratitude to all those who have provided such a useful feedback through their comments on the earlier editions of this work.

UWIST

PJFG
JDRT

1983

Preface to second edition (1975 impression)

This impression is based on the International System of Units (Système International d'Unités-SI) in that the various examples are generally worked out in terms of basic and derived SI units as set out in Sections I.3.3 to I.3.7 of *'Symbols, Signs, and Abbreviations Recommended for British Scientific Publications'* (The Symbols Committee of the Royal Society, 1969). However, some units outside the International System, such as the standard atmosphere (atm), ångström (Å), barn (b), curie (Ci), minute (min), hour (h), electron volt (eV) and unified atomic mass (u) have been retained in certain instances in accordance with the 1969 considerations of the International Committee of Weights and Measures (CIPM) as summarized in Tables 8 to 10 of *'The International System of Units'* (National Physical Laboratory: HMSO, London, 1973). Observations such as pressure (in mmHg) and temperature (in °C) given in questions have been converted to SI Units during the working-out stage.

The authors thank the examining authorities named in the preface to the first edition for permitting such amendments to be made, where necessary, to the numerical data of their questions.

UWIST

PJFG

1974

JDRT

Preface to first edition

In producing this book, the authors' aim has been to provide an illustration, by means of typical worked examples, of the calculations encountered in the study of advanced physical chemistry. Each set of worked examples in a particular branch of the subject is followed by a series of problems (with answers) to be solved by the reader.

Detailed theoretical discussion of equations used has been avoided where it was considered that an adequate treatment was to be found in current text-books of physical chemistry. In this way a wide selection of material could be made, without producing an unnecessarily bulky volume.

The authors have solved problems selected mainly from papers set in university degree examinations and in the examinations of the Royal Institute of Chemistry and the Pharmaceutical Society. In a number of instances the problems are based on data taken from original papers, to which full reference is made.

The authors wish to thank the Royal Institute of Chemistry, the Pharmaceutical Society and the authorities of the following universities for permission to use questions set in their examinations:

Birmingham, Bristol, Durham, Glasgow, Leeds, Liverpool, London, Nottingham, Queen's University of Belfast, Sheffield, Southampton and Wales.

PJFG

JDRT

April 1962

Constants and Conversion Factors

EXCEPT where otherwise stated, the following values for constants and conversion factors have been used throughout this book:

1 atmosphere	760 mmHg
	$1.013 \times 10^5 \text{ N m}^{-2}$
Molar gas constant (R)	8.31 J K^{-1}
Boltzmann constant (k)	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Molar volume of gas at s.t.p.	22.4 dm^3
Avogadro constant (L)	$6.02 \times 10^{23} \text{ mol}^{-1}$
0°C	273 K
Faraday (F)	$96\,500 \text{ coulombs (C)}$
$\frac{2.303 RT}{F}$	0.0591 V
Acceleration of gravity (g)	9.81 m s^{-2}
Planck constant (h)	$6.624 \times 10^{-34} \text{ J s}$
Velocity of light (c)	$3.00 \times 10^8 \text{ m s}^{-1}$
π	3.142
1 Ångström (Å)	$10^{-10} \text{ m (100 pm)}$
1 Debye (D)	$3.336 \times 10^{-30} \text{ C m}$
$\ln x$	$2.303 \log x$
1 Joule (J)	1 N m
1 Newton (N)	kg m s^{-2}

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1

First Law of Thermodynamics

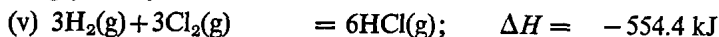
Example 1.1 Hess' law of constant heat summation

From the following data, calculate the heat of formation of anhydrous aluminium chloride:

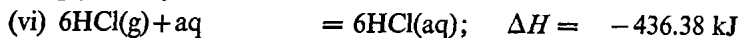
- (i) $2\text{Al}(s) + 6\text{HCl}(aq) = \text{Al}_2\text{Cl}_6(aq) + 3\text{H}_2(g); \quad \Delta H = -1007 \text{ kJ}$
- (ii) $\text{H}_2(g) + \text{Cl}_2(g) = 2\text{HCl}(g); \quad \Delta H = -184.8 \text{ kJ}$
- (iii) $\text{HCl}(g) + aq = \text{HCl}(aq); \quad \Delta H = -72.73 \text{ kJ}$
- (iv) $\text{Al}_2\text{Cl}_6(s) + aq = \text{Al}_2\text{Cl}_6(aq); \quad \Delta H = -645.5 \text{ kJ}$

This is a straightforward example involving the application of Hess' law of constant heat summation. However, the symbol 'aq' often presents difficulty to students. This symbol merely indicates that sufficient water is present to produce a solution which has a negligible or zero heat of dilution and is NOT to be treated as a molecular proportion, that is, '1 aq' is treated as equal to '2 aq' or any other number of 'aq' as illustrated by the multiplication of equation (iii) by 6 to give equation (vi) below.

Multiply (ii) by 3.



Multiply (iii) by 6.



Add (i), (v) and (vi).



Subtract (iv) from (vii).



By equation (viii), the heat of formation ($-\Delta H$) of aluminium chloride is 1352 kJ.

Example 1.2 The Kirchhoff equation

The heat of formation of one mole HI (gas) from hydrogen and iodine vapour at 25°C is 33.6 kJ (endothermic). Find the heat of

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formation at 10°C given that the heat capacities ($\text{J K}^{-1} \text{ mol}^{-1}$) of hydrogen, iodine vapour and HI vapour are given by the equations:

$$\text{Hydrogen:} \quad C_p = 27.3 + 0.0071 T;$$

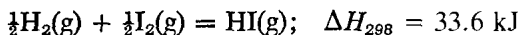
$$\text{Iodine vapour:} \quad C_p = 27.3 + 0.0160 T;$$

$$\text{Hydrogen iodide gas:} \quad C_p = 27.3 + 0.0067 T;$$

where T is the thermodynamic (absolute) temperature.

(B.Pharm., London)

From the given data, it may be written:



The general expression for the change in heat capacity (ΔC_p) accompanying the reaction, in the temperature range for which the heat capacity data are applicable, is given by:

$$\begin{aligned} \Delta C_p &= C_{p(\text{HI})} - \frac{1}{2}[C_{p(\text{H}_2)} + C_{p(\text{I}_2)}] \text{ J K}^{-1} \\ &= 27.3 + 0.0067T - \frac{1}{2}[27.3 + 0.0071T + 27.3 + 0.0160T] \text{ J K}^{-1} \\ &= -0.00485T \text{ J K}^{-1} \end{aligned}$$

The Kirchhoff equation relates ΔH_{283} to ΔH_{298} .

$$\Delta H_{298} = \Delta H_{283} + \int_{283}^{298} \Delta C_p dT$$

(the temperatures, including integration limits, being shown in K)

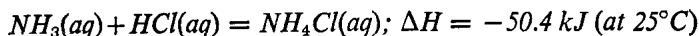
$$\text{Therefore } 33\,600 = \Delta H_{283} - 0.00485 \int_{283}^{298} T dT \text{ J}$$

$$\begin{aligned} \text{and } \Delta H_{283} &= 33\,600 + \frac{0.00485}{2} \left[T^2 \right]_{283}^{298} \text{ J} \\ &= 33\,600 + \frac{0.00485}{2} [298^2 - 283^2] \text{ J} \\ &= 33\,621 \text{ J} \end{aligned}$$

The heat of formation ($-\Delta H$) of 1 mole of HI (gas) at 10°C is -33.62 kJ .

Example 1.3 Hess' law of constant heat summation and the Kirchhoff equation

(a) Calculate the heat of formation (x) of gaseous hydrogen chloride at 25°C using the following data:



Substance	$\text{NH}_3(\text{gas})$	$\text{HCl}(\text{gas})$	$\text{NH}_4\text{Cl}(\text{solid})$
Heat of formation (ΔH) at $25^\circ\text{C}/\text{kJ mol}^{-1}$	-46.2	(x)	-315
Heat of solution (ΔH) at $25^\circ\text{C}/\text{kJ mol}^{-1}$	-35.7	-73.5	+16.4

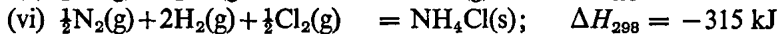
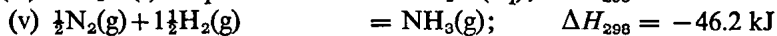
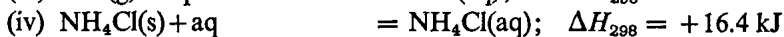
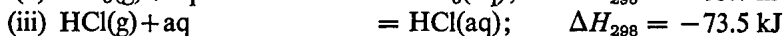
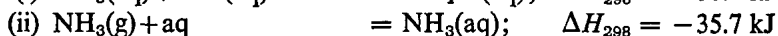
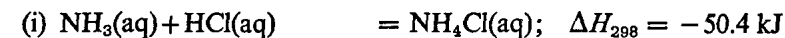
(b) Use the result of (a) and the following heat capacity equations to calculate the heat of formation of gaseous hydrogen chloride at 727°C .

$$\text{H}_2(\text{gas}): C_p = 27.8 + 3.4 \times 10^{-3}T (\text{J K}^{-1} \text{mol}^{-1})$$

$$\text{Cl}_2(\text{gas}): C_p = 34.8 + 2.4 \times 10^{-3}T (\text{J K}^{-1} \text{mol}^{-1})$$

$$\text{HCl}(\text{gas}): C_p = 28.1 + 3.5 \times 10^{-3}T (\text{J K}^{-1} \text{mol}^{-1}) \quad (\text{R.S.C.})$$

(a) From the information given, it may be written:

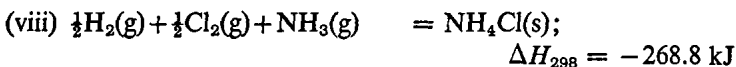


By the application of Hess' law of constant heat summation, the heat of formation of gaseous hydrogen chloride may be found as follows:

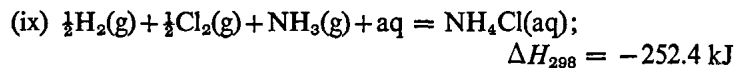
Add equations (i), (ii) and (iii).



Subtract (v) from (vi).



Add (viii) and (iv).



Subtract (vii) from (ix).



By equation (x) the heat of formation of gaseous hydrogen chloride at 25°C is 92.8 kJ mol^{-1} evolved, that is, ΔH is negative.

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(b) For the reaction

$\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) = \text{HCl}(\text{g})$; at 298 K and 1000 K, we have, according to Kirchhoff's law

$$\Delta H_{298} + \int_{298}^{1000} C_{p(\text{HCl})} dT = \Delta H_{1000} + \int_{298}^{1000} [\frac{1}{2}C_{p(\text{H}_2)} + \frac{1}{2}C_{p(\text{Cl}_2)}] dT \text{ J}$$

$$\text{or} \quad \Delta H_{1000} = \Delta H_{298} + \int_{298}^{1000} \Delta C_p dT \text{ J}$$

where

$$\begin{aligned} \Delta C_p &= C_{p(\text{HCl})} - \frac{1}{2}[C_{p(\text{H}_2)} + C_{p(\text{Cl}_2)}] \text{ J K}^{-1} \\ &= 28.1 + 3.5 \times 10^{-3}T - \frac{1}{2}[27.8 + 3.4 \times 10^{-3}T \\ &\quad + 34.8 + 2.4 \times 10^{-3}T] \text{ J K}^{-1} \\ &= -3.2 + 0.6 \times 10^{-3}T \text{ J K}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta H_{1000} &= -92\,800 + \int_{298}^{1000} (-3.2 + 0.6 \times 10^{-3}T) dT \text{ J} \\ &= -92\,800 + \left[-3.2T + \frac{0.6 \times 10^{-3}T^2}{2} \right]_{298}^{1000} \text{ J} \\ &= -94\,773 \text{ J} \end{aligned}$$

The heat of formation of gaseous hydrogen chloride at 727°C is 94.8 kJ mol⁻¹ evolved.

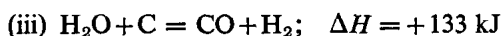
Example 1.4 Hess' law of constant heat summation

The heats of formation of carbon monoxide and steam are 111 and 244 kJ respectively. Calculate (a) the heat of the reaction: $\text{H}_2\text{O} + \text{C} = \text{CO} + \text{H}_2$, and (b) the proportion by volume, of air and steam which, if passed into a mass of coke at about 1000°C, will maintain a constant temperature. A 20% allowance for dissipation (by radiation, etc.) of heat produced in the reaction with oxygen is to be assumed. (University of Durham)

From the information given, we can formulate

- (i) $\text{C} + \frac{1}{2}\text{O}_2 = \text{CO}; \quad \Delta H = -111 \text{ kJ}$
and (ii) $\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}; \quad \Delta H = -244 \text{ kJ}$

(a) The heat of the reaction: $\text{H}_2\text{O} + \text{C} = \text{CO} + \text{H}_2$ can now be determined by subtracting (ii) from (i) (by Hess' law of constant heat summation) to give



(b) A mass of coke is to be maintained at 1000°C by allowing air and steam to pass into it, that is, by allowing the exothermic reaction (i) to occur along with the endothermic reaction (iii). 20% of the heat produced by (i) is assumed to be dissipated.

Therefore, effectively, the decrease in heat content ($-\Delta H$) per mole of carbon monoxide produced by (i) is 88.8 kJ, that is, $\Delta H = -88.8 \text{ kJ}$.

To maintain constant temperature, the heat required for the endothermic reaction (iii) must balance that produced in the exothermic reaction (i).

Hence the proportion, by volume, of steam and oxygen required is

$$\text{One part of steam to } \frac{1}{2} \times \frac{133}{88.8} \text{ parts of oxygen.}$$

And the proportions, by volume, of steam and air required are

$$\begin{aligned} \text{One part of steam to } 5 \times \frac{1}{2} \times \frac{133}{88.8} \text{ parts of air.} \\ = 3.74 \text{ parts of air.} \end{aligned}$$

Summary (a) The heat ($-\Delta H$) of the reaction $\text{H}_2\text{O} + \text{C} = \text{CO} + \text{H}_2$ is -133 kJ .

(b) The proportion, by volume, of air and steam which, if passed into a mass of coke to maintain a constant temperature of about 1000°C , assuming a 20% allowance for dissipation, is

One part of steam to 3.74 parts of air.

Example 1.5 Calculation of bond energy and resonance energy

What do you understand by the terms 'bond energy' and 'resonance energy'?

The heat of formation of methane from solid carbon and gaseous molecular hydrogen is 74.8 kJ . The heat required to convert 1 mol of hydrogen into atoms is 436 kJ and that required to convert 1 mol of solid carbon into atoms may be assumed to be 717 kJ . Calculate the heat of formation of methane from gaseous atoms.

The heats of formation of ethane, ethene and benzene from gaseous atoms are 2839, 2275, and 5509 kJ respectively. Calculate the resonance energy of benzene compared with one Kekulé structure.

(B. Pharm., Nottingham)

'Bond energy' is the average amount of energy, per mole, required to break a bond and separate the resulting atoms from each other. Thus, one quarter of the energy required to dissociate 1 mole of methane into atomic carbon and hydrogen is taken as the bond energy of the C—H linkage. Equation (v) below shows that the energy required to dissociate 1 mole of methane into gaseous atoms, that is, to break four C—H bonds, is 1664 kJ. Hence, the C—H bond energy,

$$E_{\text{C-H}} = \frac{1664}{4} = 416 \text{ kJ}$$

Because of resonance, the benzene molecule, for example, has a lower energy and greater stability than any of its resonating structures. Hence, its heat of formation from its gaseous atoms will be greater than that of a resonating structure, such as a Kekulé structure. The extra energy given out is the 'resonance energy'.

Calculation of the heat of formation of methane from gaseous atoms

From the information given, it may be written:

- (i) $\text{C(s)} + 2\text{H}_2(\text{g}) = \text{CH}_4(\text{g}); \quad \Delta H = -74.8 \text{ kJ}$
- (ii) $\text{H}_2(\text{g}) = 2\text{H(atoms, g)}; \quad \Delta H = 436 \text{ kJ}$
- (iii) $\text{C(s)} = \text{C(atoms, g)}; \quad \Delta H = 717 \text{ kJ}$

By the application of Hess' law of constant heat summation, the heat of formation of methane from gaseous atoms may be found as follows:

Multiply (ii) by 2 and add to (iii).

- (iv) $\text{C(s)} + 2\text{H}_2(\text{g}) = 4\text{H(atoms, g)} + \text{C(atoms, g)}; \quad \Delta H = 1589 \text{ kJ}$

Subtract (i) from (iv).

- (v) $4\text{H(atoms, g)} + \text{C(atoms, g)} = \text{CH}_4(\text{g}); \quad \Delta H = -1664 \text{ kJ}$

By equation (v), the heat of formation of methane from gaseous atoms is 1664 kJ mol⁻¹ (evolved).

Calculation of resonance energy of benzene

To evaluate the resonance energy of benzene from the given data, it is first necessary to evaluate the energies of the C—H, C=C, and C—C bonds, and then to calculate the heat of formation of a Kekulé structure,

which is subtracted from the given heat of formation of benzene to yield the resonance energy.

The C—H bond energy, as shown above, is 416 kJ

Ethane contains 6 C—H bonds and 1 C—C bond. Hence, the energy absorbed in the dissociation of ethane into gaseous atoms, that is, 2839 kJ, will be equal to the sum of these bond energies:

$$6E_{\text{C-H}} + E_{\text{C-C}} = 2839 \text{ kJ}$$

$$\begin{aligned} \text{Therefore } E_{\text{C-C}} &= 2839 - 6 \times 416 \text{ kJ} \\ &= 343 \text{ kJ} \end{aligned}$$

Therefore, the C—C bond energy is 343 kJ.

Ethene contains 4 C—H bonds and 1 C=C bond. Hence, the energy absorbed in the dissociation of ethene to gaseous atoms, that is, 2275 kJ, will be equal to the sum of these bond energies:

$$4E_{\text{C-H}} + E_{\text{C=C}} = 2275 \text{ kJ}$$

$$\begin{aligned} \text{Therefore } E_{\text{C=C}} &= 2275 - 4 \times 416 \text{ kJ} \\ &= 611 \text{ kJ} \end{aligned}$$

Therefore the C=C bond energy is 611 kJ.

The heat of formation of a Kekulé structure from gaseous atoms will be equal to the heat liberated on the formation of 3 C=C, 6 C—H, and 3 C—C bonds.

That is, the heat of formation of a Kekulé structure is given by

$$\begin{aligned} 3E_{\text{C=C}} + 6E_{\text{C-H}} + 3E_{\text{C-C}} &= 1833 + 2496 + 1029 \text{ kJ} \\ &= \underline{5358 \text{ kJ}} \end{aligned}$$

The observed heat of formation of benzene from its elements is 5509 kJ and hence the resonance energy is equal to

$$5509 - 5358 = 151 \text{ kJ}$$

The resonance energy of benzene, compared with one Kekulé structure, is 151 kJ mol⁻¹.

Example 1.6 The Born-Haber cycle

From the data given below draw an energy cycle and from it calculate the lattice energy of lithium chloride.

Enthalpy of atomization of lithium, $(\text{Li}(s) \rightarrow \text{Li}(g))$,

$$\Delta H = +159 \text{ kJ mol}^{-1}$$

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Dissociation energy of chlorine, ($\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$),

$$\Delta H = +121 \text{ kJ mol}^{-1} \text{ of Cl (g)}$$

Ionization energy of lithium, ($\text{Li}(\text{g}) \rightarrow \text{Li}^+(\text{g}) + e^-$),

$$\Delta H = +520 \text{ kJ mol}^{-1}$$

Electron affinity of chlorine, ($\text{Cl}(\text{g}) + e^- \rightarrow \text{Cl}^-(\text{g})$),

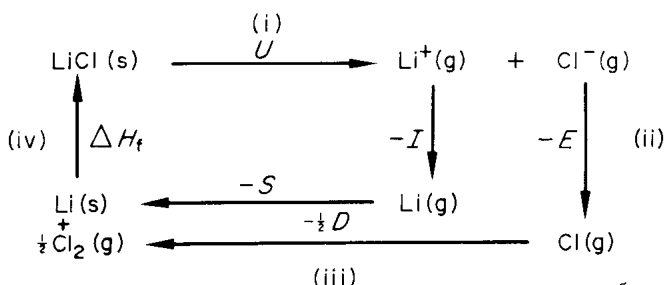
$$\Delta H = -370 \text{ kJ mol}^{-1}$$

Enthalpy of formation of lithium chloride, ($\text{Li}(\text{s}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{LiCl}(\text{s})$),

$$\Delta H = -402 \text{ kJ mol}^{-1}$$

(G.C.E. 'A' Level (Nuffield), London)

The Born-Haber cycle is an energy cycle which presents a breakdown pattern of compounds possessing an *ideal* electrovalency. It collates in a simple quantitative manner several fundamental enthalpic energy quantities (that is, of the ΔH type), as illustrated by the data of this question:



In the cycle, the first step (i) is the complete break-up of the lithium chloride crystal, $\text{LiCl}(\text{s})$, into gaseous Li^+ and Cl^- ions. This is accompanied by an increase in the enthalpy (heat content), $\Delta H_{(i)}$, which is the *lattice energy*, U .

The second operation (ii) is the simultaneous discharging of the metal Li^+ ions and of the Cl^- ions. This stage is accompanied by an enthalpy change, $\Delta H_{(ii)}$, corresponding to $-(E - I)$, where E is the electron affinity of the Cl atom and I is the ionization energy of the Li atom.

In the third step (iii), the gaseous lithium is condensed to the solid state and the chlorine atoms are combined to give Cl_2 molecules, the processes being accompanied by a change in enthalpy, $\Delta H_{(iii)}$, corresponding to the sum of $-S$, that is, minus the *enthalpy of atomization*

of lithium, and of $-\frac{1}{2}D$, that is, minus one half of the *dissociation enthalpy* (or *energy*) of molecular chlorine.

The final step (iv) corresponds to the interaction of the solid lithium with gaseous Cl_2 molecules, that is, in the forms they normally exist at 298 K, to reform the crystalline lithium chloride. The attendant enthalpy change, $\Delta H_{(\text{iv})}$, is the *enthalpy of formation*, ΔH_f , of the lithium chloride. All the other quantities referred to in the cycle are also for 298 K.

By Hess' law of constant heat summation

$$\Delta H_{(\text{i})} + \Delta H_{(\text{ii})} + \Delta H_{(\text{iii})} + \Delta H_{(\text{iv})} = 0$$

$$\text{that is, } U - E - I - S - \frac{1}{2}D + \Delta H_f = 0 \quad (1)$$

The value of any quantity in equation (1) may be calculated, provided the other five are known. Information on five of the six quantities is given in the question, hence the value of the sixth, namely the lattice energy of lithium chloride (U), may be calculated by substituting the appropriate data in equation (1):

$$U = -370 + 520 + 159 + 121 + 402 \text{ kJ mol}^{-1} = \underline{\underline{+832 \text{ kJ mol}^{-1}}}$$

Example 1.7 Reversible isothermal expansion

2 dm^3 of hydrogen, initially at s.t.p., are expanded isothermally and reversibly to a volume of 4 dm^3 . Calculate the work done.

Since 22.4 dm^3 is the volume occupied by 1 mole at s.t.p., 2 dm^3 is the volume occupied by $1 \times \frac{2}{22.4}$ mole at s.t.p. The work done (W)

in the isothermal, reversible expansion of 1 mole of an ideal gas is given by:

$$W = RT \ln \frac{V_2}{V_1} \text{ J} \quad \text{where } V_1 \text{ and } V_2 \text{ are the initial and final gas volumes.}$$

Assuming ideal behaviour by the hydrogen, the work done in the expansion of 2 dm^3 of the gas to a volume of 4 dm^3 will, therefore, be given by

$$W = \frac{2}{22.4} RT \ln \frac{V_2}{V_1} = \frac{2 \times 8.31 \times 273}{22.4} \ln \frac{4}{2} = \underline{\underline{140.5 \text{ J}}}$$

Example 1.8 Reversible adiabatic expansion of an ideal gas

Two moles of an ideal gas ($C_p = 12.5 \text{ J K}^{-1} \text{ mol}^{-1}$) at 300 K are compressed adiabatically to one quarter of the original volume; what is the temperature of the gas after compression? (B. Pharm., London)