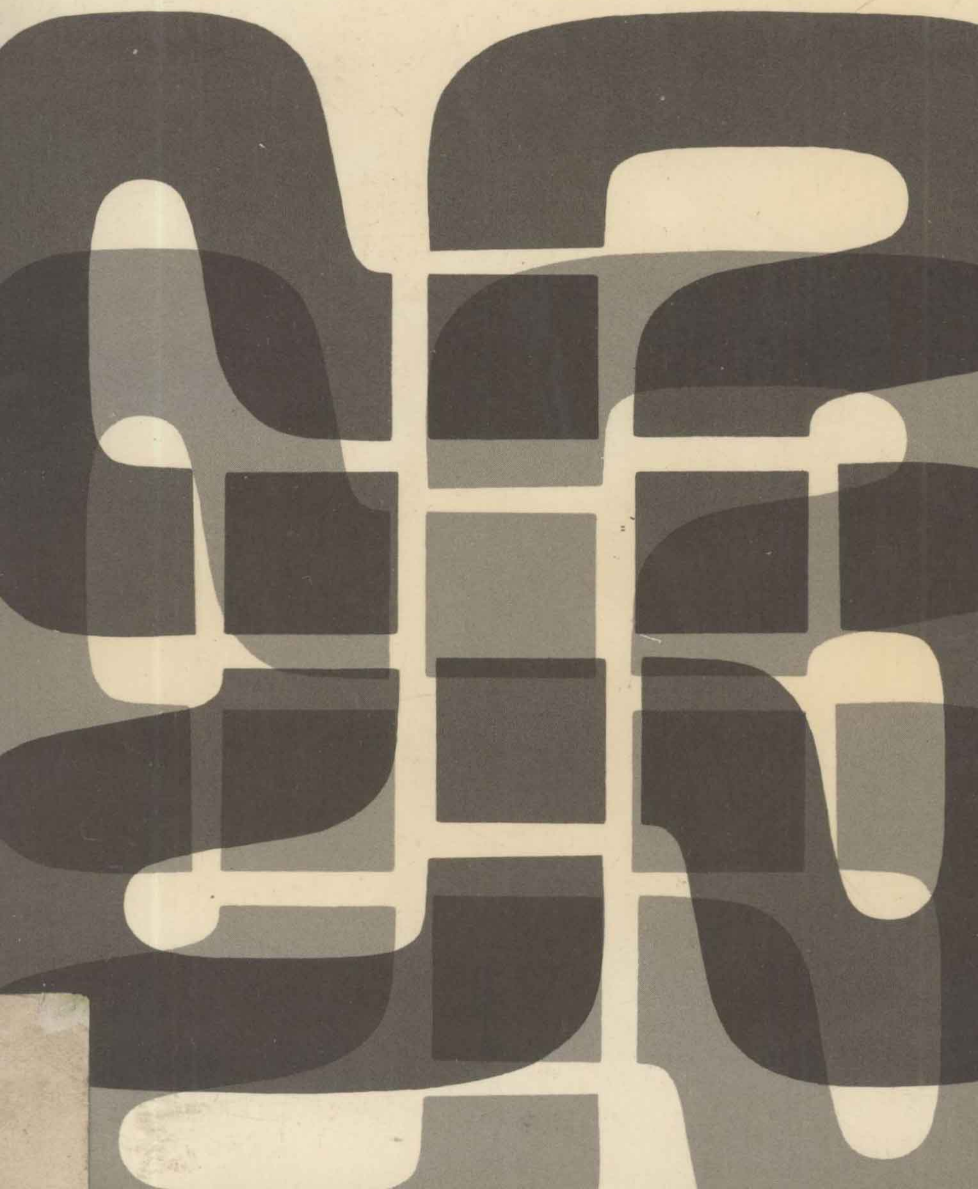
Problems in Physical Chemistry

A. WOOD



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Preface

I believe that a proper appreciation and understanding of the principles of physical chemistry depends to a considerable extent upon working with the material normally supplied in the form of lectures and reading material. This working may take the form of directed tutorials, laboratory exercises, or private or group study; but the solution of numerical problems is always required, and it is essential in the necessary familiarization processes. Many of the exercises given in this book have been used in examinations and tutorials. This book is not designed to replace lectures and textbook study, but to supplement them: for this reason theoretical preamble and model questions and answers have been excised – the space saved by the latter economy has been used to provide a skeletal solution to each problem and suggestions for working. The student should provide himself with his recommended textbook and an adequate set of tables (in SI units). References are provided in many cases. The exercises are relevant to the later years of tertiary chemistry, but introductory material has been incorporated also, so that the book may be used from the earliest stages and retained throughout the course. Suggestions for improvements and extensions of the coverage would be welcome and I should be pleased if readers finding any errors would let me know.

Liverpool, 1974 A.W.

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Contents

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1. THERMODYNAMICS 1
   - 1.1. Real and ideal gases. 1
   - 1.2. Kinetic theory of gases. 9
   - 1.3. Thermochemistry. 11
   - 1.4. Chemical equilibria in the gas phase and in solution. 15
   - 1.5. Use of heat capacity data. 19
   - 1.6. Use of the Clapeyron and derived equations. 21
   - 1.7. Use of the van't Hoff isochore and isotherm. 23
   - 1.8. Use of the Planck isotherm. 24
   - 1.9. Multicomponent homogeneous phases. 25
   - 1.10. Activities in homogeneous condensed phases. 27
   - 1.11. Use of Gibbs function functions. 29
   - 1.12. Partition functions. 29
   - 1.13. Differential thermodynamic relationships. 30
   - 1.14. Supplementary. 32

2. PHASE EQUILIBRIA 35
   - 2.1. Applications of Gibbs phase rule. 35
   - 2.2. Unary systems. 35
   - 2.3. Binary systems: solid–liquid. 37
   - 2.4. Binary systems: liquid–vapour. 39
   - 2.5. Ternary systems. 41
   - 2.6. Supplementary. 43

3. ELECTROCHEMISTRY 45
   - 3.1. Activity and ionic strength. 45
   - 3.2. Salt solubility and ionic strength. 46
   - 3.3. Dissociation of acids and bases: buffer solutions. 47

3.4. Cells without transport. 49
3.5. Concentration cells. 51
3.6. Transport numbers. 52
3.7. Titrations. 54
3.8. Ion-selective electrodes. 57
3.9. Polarography. 57
3.10. E.m.f.'s and thermodynamics. 59
3.11. Colligative properties (electrolytes). 61
3.12. Supplementary. 62

4. KINETICS 64
4.1. First order reactions. 64
4.2. Second order reactions. 66
4.3. Dependence of reaction rate upon temperature. 68
4.4. Analysis of kinetic data. 69
4.5. Reaction mechanisms. 71
4.6. Kinetics and photochemistry. 74
4.7. Applications of isotopes in kinetics. 75
4.8. Supplementary. 77

5. SURFACE CHEMISTRY 80
5.1. Adsorption isotherms. 80
5.2. Micelle formation. 81
5.3. Supplementary. 82

6. CRYSTALLOGRAPHY 84
6.1. Crystal systems and classes. 84
6.2. Miller indices. 84
6.3. Lattice dimensions and related measurements. 85
6.4. X-ray crystallography. 86

7. QUANTUM CHEMISTRY AND SPECTROSCOPY 88
7.1. Operations in quantum mechanics. 88
7.2. The infrared: rotational and vibrational–rotational spectra. 88
7.3. Thermodynamic properties. 89
7.4. Supplementary. 89

8. SPECTROPHOTOMETRY 92
8.1. Use of absorption data. 92
REFERENCES 95
SOLUTIONS 101

1

Thermodynamics

1.1. Real and ideal gases

1.1.1. The vapour pressure of both solid and liquid $SbBr_3$ has been obtained at selected temperatures by a transpiration method using argon as the carrier gas. Find the vapour pressure of $SbBr_3$ from the following data.

T/K	375·7	377·7	385·2	389·2	395·2	399·7
Ar transpired/mmol	40·8	22·9	21·0	28·0	29·2	24·0
Sb transpired/μmol	60·5	34·8	52·7	73·0	107·0	112·6

Total pressure was 99·5 kN m^{-2}. Assume that the gases are ideal, that the argon is saturated with $SbBr_3$, and that the transport of $SbBr_3$ by thermal diffusion (from the hot end of the transport tube to the cold end) is negligible.

1.1.2. The coefficient of thermal expansion of hydrogen in the temperature range 273 K to 473 K is given below as a function of pressure.

p/kN m^{-2}	1·333	2·666	4·000	5·333	6·666
$\alpha \times 10^6$/K^{-1}	3635	3610	3584	3559	3532

Estimate a value for the temperature of absolute zero.

1.1.3. (*a*) The density of acetylene gas, as a function of pressure at 200 K, has been obtained, with the results shown below.

p/kN m^{-2}	10·13	20·27	30·40	50·66	70·93	101·325
ρ/kg m^{-3}	0·1590	0·3188	0·4795	0·8031	0·1130	0·1627

Find the relative molecular mass of acetylene from these figures.

(*b*) The density of acetylene gas as a function of pressure has been obtained, also at 250 K.

p/kN m^{-2}	10·13	20·27	30·40	50·66	70·93	101·325
ρ/kg m^{-3}	0·1270	0·2544	0·3821	0·6385	0·8960	0·1285

Find the relative molecular mass of acetylene from these figures and compare it with the value obtained from part (*a*).

1.1.4. Using the barometric formula, estimate the barometric pressure at the top of Ben Nevis (height 1343 m) on a day when the atmospheric pressure at sea level was 100 kN m^{-2}. Assume that the air temperature is uniform at 273·2 K, and that there are no turbulence effects. Take the effective relative molecular mass of air to be 28·8.

1.1.5. Calculate the work done when 1 mole of a gas (assumed ideal) expands (*a*) reversibly and isothermally from 400 kN m^{-2} to 150 kN m^{-2}, and (*b*) irreversibly and isothermally from 400 kN m^{-2} to 150 kN m^{-2}, in one stage, by a sudden direct reduction of pressure to 150 kN m^{-2}. $T = 298{\cdot}15$ K. Show the work done in each case, using a sketched Indicator Diagram. How much heat is absorbed in each case and what changes occur in the internal energy and enthalpy?

1.1.6. Calculate the external work done when vaporizing 1 kg of water under the following conditions (the volume of the liquid phase may be neglected).

T/K	323·15	373·15	423·15	473·15
vapour pressure/kN m^{-2}	12·30	101·325	475·79	1552·8
Specific volume of steam/m^3 kg^{-1}	12·02	1·671	0·3921	0·1274

Find also the internal energy change in each case, given that the enthalpies of vaporization are 2378·2, 2253·9, 2109·2 and 1940·5 kJ kg^{-1} respectively.

1.1.7. (*a*) Calculate the work done and the final temperature reached when a quantity of gas (which may be assumed to be ideal) is expanded adiabatically and irreversibly to equilibrium against a constant external pressure of 101·325 kN m^{-2}. Initial gas pressure is 2·533 MN m^{-2}: initial temperature is 300·15 K.

(*b*) One mole of an ideal diatomic gas (i.e. $U = \frac{5}{2} RT$) is expanded irreversibly and adiabatically in one stage from 1013·25 kN m^{-2} and 273·15 K against a constant pressure of 101·325 Kn m^{-2}. What is the final temperature? Calculate also the work done, the change in internal energy and the change in enthalpy.

1.1.8. (*a*) Show that the work done in the reversible adiabatic expansion of *n* moles of an ideal gas is given by,

$$w = \frac{p_1V_1 - p_2V_2}{\gamma - 1}.$$

(*b*) Calculate the final temperature and the work done when 2 moles of an ideal gas are expanded adiabatically and reversibly from 5 dm^3 at 300 K to a final volume of 40 dm^3.

(*c*) Calculate the work done when 1 mole of an ideal diatomic gas is expanded reversibly and adiabatically from 1·013.25 kN m^{-2} and 273·15 K to 101·325 kN m^{-2}. What is the final temperature?

1.1.9. (*a*) The van der Waals constants for gaseous ammonia are $a = 0{\cdot}4225$ N m^4 mol^{-2} and $b = 0{\cdot}0371$ dm^3 mol^{-1} in the usual notation. Calculate the pressure of this gas when 5 moles of it are compressed to 10 dm^3 at 473·15 K.

(*b*) Calculate the pressure required to contain the same 5 moles of ammonia gas in a volume of 2 dm^3 at the same temperature (*i*) assuming the gas is ideal, and (*ii*) as found using the van der Waals equation.

1.1.10. The compression factor for air is represented by unity at 273·15 K and 101·325 kN m^{-2}, and by 1·3951 at 373·15 K and 10·1325 MN m^{-2}. A certain quantity of air, occupying 10 dm^3 at 273·15 K and 101·325 kN m^{-2}, is heated and compressed to 373·15 K and 10·1325 MN m^{-2}. Calculate the final volume, and compare it with the value obtained from the ideal gas laws.

1.1.11. If the standard entropy of liquid water at 298·15 K is 69·96 J K^{-1} mol^{-1}, calculate the entropy of water vapour in its standard state (i.e. in the hypothetical state of a gas at 298·15 K and under 101·325 kN m^{-2} pressure). The vapour pressure of water is 3·168 kN m^{-2} at 298·15 K and its enthalpy of vaporization is 2·436 kJ g^{-1}.

1.1.12. A gas, assumed ideal is expanded from 2·5 MN m^{-2} at 400 K to 100 kN m^{-2} at 300 K. If the initial volume was 100 dm^3, find (*i*) the number of moles, (*ii*) the final volume, (*iii*) ΔH, (*iv*) ΔU and (*v*) ΔS.

1.1.13. The vapour pressure of water is 3·1672 kN m^{-2} at 298·15 K. Calculate the Gibbs function of formation of water vapour in the hypothetical state of a gas at this temperature, and under a pressure of 101·325 kN m^{-2}, given that the standard Gibbs function of formation of liquid water is −237·2 kJ mol^{-1}.

1.1.14. Find q, w, ΔU, ΔH, ΔS, ΔG, and ΔA for 1 mole of an ideal gas expanded isothermally and irreversibly into a vacuum from initial volume V_1 to final volume V_2. Find also ΔS for (*a*) the surroundings, and (*b*) the whole universe.

1.1.15. (*a*) Find an expression for the maximum work done by a real gas whose equation of state is $p(V/n-b) = RT$, in an isothermal expansion from V_1 to V_2.

(*b*) What is the work done by a gas in an isothermal expansion if the equation of state for the gas is,

$$p\frac{V}{n} = RT\left(\frac{bp}{RT} - \frac{ab}{R^3T^3}\right)?$$

1.1.16. Obtain expressions for ΔG and ΔA for the reversible isothermal expansion of a gas whose behaviour can be described by,

$$p\frac{V}{n} = RT + ap.$$

1.1.17. The heat capacity of a certain gas at constant volume is given by the expression,

$$C_V = g + hT.$$

If the van der Waals equation of state, with $a = 0$, can be used to describe this gas, obtain an expression for the entropy change, ΔS, occurring when 1 mole of the gas is transferred from state (p_1, V_1, T_1) to state (p_2, V_2, T_2). (Assume g and h are not functions of volume).

1.1.18. Estimate the critical temperatures of the following compounds from their van der Waals constants.

	$a/N\ \mathrm{m}^4\ \mathrm{mol}^{-2}$	$b/\mathrm{dm}^3\ \mathrm{mol}^{-1}$
Benzene	1·824	0·1154
Fluorobenzene	2·019	0·1286
Naphthalene	4·027	0·1937
n-Octane	3·781	0·2368
n-Pentane	1·026	0·1460
n-Propylbenzene	3·633	0·2028
Toluene	2·438	0·1463

1.1.19. Starting from the Clausius equation of state for a real gas,

$$\left\{p + \frac{a}{T\left(\frac{V}{n}+c\right)^2}\right\}\left\{\frac{V}{n} - b\right\} = RT,$$

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obtain expressions for the critical pressure, critical temperature and critical volume. Obtain also a formula for the compression factor at the critical point.

1.1.20. Calculate the Boyle temperatures for ethane and propane, given the following van der Waals data;

	$a/\mathrm{N\,m^4\,mol^{-2}}$	$b/\mathrm{dm^3\,mol^{-1}}$
Ethane	0·5562	0·06380
Propane	0·8779	0·08445

1.1.21. Using the Berthelot equation of state for real gases, derive an expression for the Boyle temperature.

1.1.22. A certain gas has a reduced temperature of 1⅓ and a reduced pressure of 1. Show that its reduced voluem is 3, and calculate its compression factor under these conditions. What value is obtained from compression factor charts?

Using these charts, find also the compression factor for a gas whose reduced pressure is 2·75 and whose reduced temperature is 1·15.

1.1.23. Obtain the reduced form of the Berthelot equation of state for gases.

1.1.24. Under what circumstances does

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial p}\right)_T = \left(\frac{\partial H}{\partial V}\right)_T = 0\ ?$$

1.1.25. Obtain Gay-Lussac's Law as a consequence of defining an ideal gas as one which (*a*) obeys Boyle's Law, and (*b*) has $(\partial U/\partial V)_T = 0$.

1.1.26. (*a*) Show that for a gas whose behaviour is described by the van der Waals equation,

$$(\partial U/\partial V)_T = n^2 a/V^2 .$$

(*b*) Show that C_V is not a function of volume for van der Waals gas.

1.1.27. (*a*) Find an expression for $(\partial U/\partial V)_T$ for a gas whose behaviour is described by the equation of state,

$$p\frac{V}{n} = RT + bp - ap/RT^2 .$$

(*b*) Find also an expression for $(\partial H/\partial p)_T$ for a gas whose behaviour is described by the above equation of state.

1.1.28. Find expressions for the partial derivatives with respect to volume of the entropy, internal energy, and enthalpy, at constant temperature, for a gas which can be described by the Berthelot equation of state.

1.1.29. See question 1.1.28. A gas is expanded adiabatically into a vacuum. If the gas obeys the Berthelot equation of state, find an expression for $(\partial T/\partial V)_U$, and derive a relationship between the initial and final temperatures and pressures. (C_V appears in the working; assume it is a constant quantity).

1.1.30. A certain gas has the equation of state

$$p\left(\frac{V}{n}-b\right) = RT.$$

Obtain an expression relating initial and final conditions for the adiabatic reversible expansion of this gas. (Assume C_V is a constant quantity).

1.1.31. Derive an expression relating initial and final states for the reversible adiabatic expansion of a van der Waals gas. (Hint: first evaluate $(\partial V/\partial T)_S$).

1.1.32. The heat capacity of a certain gas at constant volume is described by the expression,

$$C_V = k + lT + mT^2$$

and the $p-V-T$ behaviour of the gas is described by the van der Waals equation. Show that the initial and final states of a reversible adiabatic expansion are related by the expression,

$$nR\ln\left(\frac{V_2-bn}{V_1-bn}\right) = k\ln\frac{T_1}{T_2} + l(T_1-T_2) + m(T_1^2-T_2^2).$$

1.1.33. Find expressions for $(\partial S/\partial V)_T$ $(\partial S/\partial p)_T$, $(\partial U/\partial V)_T$, $(\partial H/\partial p)_T$ and $(\partial U/\partial p)_T$ for a gas whose behaviour can be described by the equation

$$p\left(\frac{V}{n}-b\right) = RT$$

Find also expressions for ΔS, ΔU, ΔH, ΔG, and ΔA for an isothermal change.

1.1.34. (*a*) The equation, $p(V/n) = RT + bp - (ap/RT^2)$ describes the behaviour of a certain gas. Show that

$$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{nC_V}{p+\dfrac{2ap^2}{R^2T^3}}$$

and

$$\left(\frac{\partial p}{\partial T}\right)_S = \frac{C_p}{\dfrac{RT}{p}+\dfrac{2a}{RT^2}}\,.$$

(*b*) Find practical expressions for $(\partial p/\partial S)_V$ and $(\partial T/\partial V)_U$.

1.1.35. Obtain an expression for α, the coefficient of thermal expansion, for a gas whose behaviour is described by the equation

$$p(V/n) = RT+bp-ap/RT^2.$$

1.1.36. Show that when a gas is described by the equation $p\dfrac{V}{n} = RT+pb-\dfrac{ap}{RT^2}$ then $C_p - C_V$ is independent of the value of b in the equation of state.

1.1.37. The molar heat capacity of hydrogen at constant pressure is given as a function of temperature by the equation

$$C_p = 29{\cdot}048 - 0{\cdot}8364 \times 10^{-3}\,(T/\mathrm{K}) + 20{\cdot}12 \times 10^{-7}\,(T/\mathrm{K})^2\ \mathrm{J\,K^{-1}\,mol^{-1}}.$$

Derive an expression for the heat capacity at constant volume, given that the van der Waals constants for hydrogen are, $a = 0{\cdot}2476$ N m^4 mol^{-2} and $b = 0{\cdot}02661$ dm^3 mol^{-1}. (Take $(1/n)\,(\partial V/\partial T)_p$ to be equal to $\dfrac{(V/n)-b}{T}+\dfrac{2a}{RT^2}$, to a good approximation).

1.1.38. Using the relations $\left(\dfrac{\partial S}{\partial p}\right)_T = -\left(\dfrac{\partial V}{\partial T}\right)_p$, and $V = \left(\dfrac{\partial H}{\partial p}\right)_T + T\left(\dfrac{\partial V}{\partial T}\right)_p$, describe how you would evaluate the quantity $[\Delta H_T]\,\dfrac{p_2}{p_1}$ for a real gas.

1.1.39. Starting from the thermodynamic equation of state

$$V = \left(\frac{\partial H}{\partial p}\right)_T + T\left(\frac{\partial V}{\partial T}\right)_p.$$

derive the expression,

$$\mu = \text{The Joule–Thomson coefficient}$$

$$= \frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p}.$$

1.1.40. Find an expression for the Joule–Thomson coefficient of a gas whose p–V–T relations are described by the equation

$$p\frac{V}{n} = RT + bp + \frac{ap}{RT^2}$$

Is there an inversion temperature?

1.1.41. Show that the inversion temperature of a gas which obeys Berthelot's equation can be expressed as,

$$\frac{9}{2\sqrt{2}}\left(1 - \frac{1}{3V_r}\right),$$

using reduced quantities.

1.1.42. The Joule–Thomson coefficient for CO_2 at 273·15 K is $1{\cdot}28 \times 10^{-5}$ N^{-1} m^2 K. Assuming this value to remain approximately constant over a sufficient range of pressures and temperatures, calculate the final temperature obtained when the gas is expanded through a porous insulated plug, from an initial pressure of 1500 kN m^{-2} to a final pressure of 100 kN m^{-2}. The initial temperature of the gas is 280 K.

1.1.43. Find an expression for the rate of change of entropy with pressure when a gas whose equation of state is $p\left(\frac{V}{n} - b\right) = RT$ is expanded through a porous plug.

1.1.44. Estimate the fugacity of N_2 at 500 K and 500 atmospheres, from the van der Waals equation,

$$(p + a/V^2)(V - b) = RT$$

$$a = 1{\cdot}39 \text{ dm}^6 \text{ atm mol}^{-2}$$

$$b = 39{\cdot}1 \text{ cm}^3 \text{ mol}^{-1}.$$

1.1.45. Compression factors have been obtained for propan-2-ol vapour at 473·2 K, as tabulated below. Using a graphical method, find the fugacity of the vapour at a pressure of 22 atmospheres.

p/atm	0	2	6	10	14	18	22
pV/RT	1	0·9794	0·9368	0·8897	0·8373	0·7768	0·7051

Using a value of 0·9797 for the fugacity coefficient at 2 atmospheres pressure, calculate the change in Gibbs function which occurs when 1 mole of propan-2-ol vapour is compressed from 2 atm pressure to 22 atm pressure at 473·2 K.

1.2. Kinetic theory of gases

1.2.1. Calculate the number of collisions per second between N_2 molecules at a pressure of 1 atmosphere and a temperature of 298 K and a surface whose area is 500 cm^2.

1.2.2. Calculate the mean free path, and the number of collisions per m^3 per second between HI molecules at 673·2 K and under the following pressures:

26·67 mN m^{-2}
53·33 mN m^{-2}
80·00 mN m^{-2}
106·7 mN m^{-2}
1333 mN m^{-2}

The collision diameter of the HI molecule may be taken to be 5·06 × 10^{-10} m.

1.2.3. Estimate the molecular diameters of the following gases from the values of the van der Waals constant given below.

	b/dm^3 mol^{-1}
CH_4	0·04278
C_2H_6	0·06380
C_3H_8	0·08445
n-Butane	0·1226

Estimate the contribution of the methyl group and the methylene group to the van der Waals diameter of the above molecules.

1.2.4. The vapour pressure of solid chromium has been studied by the Knudsen effusion technique. Calculate the associated vapour pressure from each of the following readings.

T/K	Time/s	Mass loss/mg	Orifice area/mm^2
1582	14 100	5·4	2·56
1602	16 010	10·4	2·19
1648	8810	15·0	2·57
1704	6950	25·1	2·10
1750	8480	85·9	2·57
1805	6190	118·6	2·57

The orifice was reamed to a 30° angle and may be considered to be ideal.

1.2.5. The Langmuir method of measuring vapour pressures involves determination of the rate of vaporization of a solid of known area, at a known temperature and under a high vacuum. The kinetic theory of gases is then applied, assuming that the evaporation coefficient is unity.

Find the vapour pressure of thorium metal from the following data.

T/K	1956	1815	1757
Vaporization rate/ mg cm^{-2} h^{-1}	0·1355	0·008 213	0·001 918

1.2.6. Rates of diffusion of vapour from a tube wherein the liquid is kept at a constant level have been measured and compared with theoretical values. Calculate the rate of diffusion of benzene vapour from the tube kept at 298 K and using the data supplied:

the diffusion coefficient is $9{\cdot}32 \times 10^{-6}\,\mathrm{m}^2\,\mathrm{s}^{-1}$;
the total pressure is $10{\cdot}40 \times 10^4\ \mathrm{Nm}^{-2}$;
the tube diameter is 6·1 mm;
the length of the diffusion path is 30 mm;
the vapour pressure of benzene at 298 K is $1{\cdot}28 \times 10^4\ \mathrm{Nm}^{-2}$.

1.2.7. The viscosity of carbon monoxide has been determined as shown. Calculate the collision diameter.

Viscosity/ kg m^{-1} s^{-1} $\times 10^{-5}$	0·561	1·27	1·66	2·183	2·548	2·714
T/K	81·7	194·7	273·2	399·9	500·2	550·1

1.2.8. Consider the translational motion of N molecules of a gas. Resolve the velocity of each molecule into its $x, y,$ and z components. Take the x components: assuming that the distribution of x-velocity components can be described by the Gaussian Distribution Function, derive the Maxwellian Distribution Law for this set of components,

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