SOLUTIONS MANUAL
to accompany

PHYSICAL CHEMISTRY
SEVENTH EDITION

ROBERT A. ALBERTY

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PREFACE

This manual gives solutions of the problems in the first set of the text R. A. Alberty, PHYSICAL CHEMISTRY, 7th ed., Wiley, New York, 1987, and it gives answers for the second set.

Working problems is an important part of learning physical chemistry. Not all knowledge of physical chemistry is quantitative, but much of it is. Since physical chemistry utilizes physics and mathematics to predict and interpret chemical phenomena, there are many opportunities to use quantitative methods.

The availability of hand-held electronic calculators has made it much easier to work physical chemistry problems and has made it possible to include more difficult problems.

The units of physical quantities are usually shown in solving problems in this manual. It is important to develop the habit of using units and cancelling them to obtain the units for the answer because this helps prevent errors.

In this book, as in your handwritten lecture notes, there is no distinction between italic (sloping) and roman (upright) type, but it is important to note that in the printed literature italic type is used for symbols for physical quantities and roman type is used for units.

I am indebted to many physical chemists who have recommended problems and who have suggested improvements in this SOLUTIONS MANUAL.

Robert A. Alberty

Cambridge, Massachusetts
February 1986

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PART ONE
THERMODYNAMICS

CHAPTER 1: Zeroth Law of Thermodynamics and Equations of State

1.1 The perfect gas law also represents the behavior of mixtures of gases at low pressures. The volume is then interpreted as the molar volume of the mixture, that is the volume of a mole of the mixture. The partial pressure of gas i in a mixture is defined as y_iP, where y_i is its mole fraction, and P is the total pressure. Ten grams of N_2 is mixed with 5 g of O_2 and held at 25 °C at 0.750 bar. (a) What are the mole fractions of N_2 and O_2? (b) What are the partial pressures of N_2 and O_2? (c) What is the molar volume assuming the molecules do not interact? (d) What is the actual volume assuming the molecules do not interact?

SOLUTION

$$m_{N_2} = \frac{10\ g}{28.013\ g\ mol^{-1}} = 0.357\ mol$$

$$m_{O_2} = \frac{5\ g}{32,000\ g\ mol^{-1}} = 0.156\ mol$$

$$P_{N_2} = (0.357/0.513)(0.750\ bar) = 0.522\ bar$$

$$P_{O_2} = (0.156/0.513)(0,750\ bar) = 0.228\ bar$$

$$V = \frac{RT}{P} = \frac{(8.3144\ J\ K^{-1}\ mol^{-1})(298.15\ K)}{0.750 \times 10^5\ Pa}$$

$$= 0,0331\ m^3\ mol^{-1}$$

The gas contains 0.357 + 0.156 = 0.513 mol and so the actual volume is (0.513 mol)(0.0331 m^3 mol^{-1}).

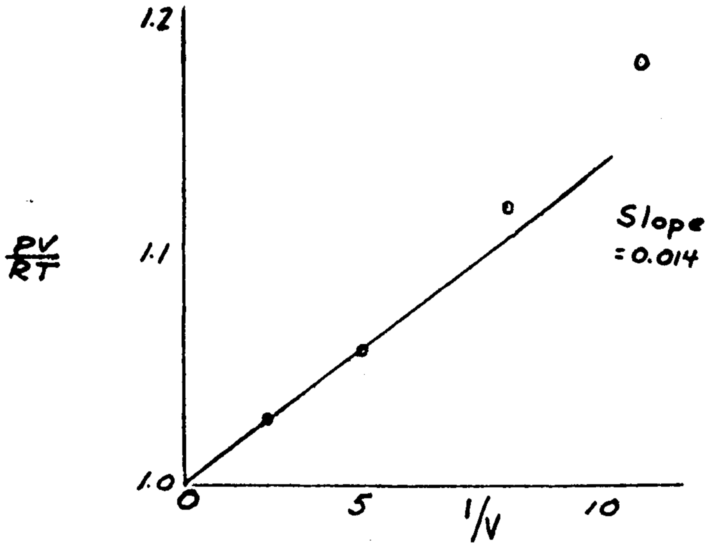
$= 0.0170\ m^3$ or 17.0 L

1.2 Calculate the second virial coefficient of hydrogen at 0 °C from the fact that the molar volumes at 50.7, 101.3, 202.6, and 303.9 bar are 0.4634, 0.2386, 0.1271, and 0.09004 L mol^{-1}, respectively.

SOLUTION

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \cdots$$

P/bar	50.7	101.3	202.6	303.9
V/L mol^{-1}	0.4634	0.2386	0.1271	0.09004
PV/RT	1.035	1.064	1.134	1.205
(1/V)/mol L^{-1}	2.158	4.191	7.868	11.106



Slope = B
= 0.014 L mol^{-1}

1.3 The second virial coefficient B of methyl isobutyl ketone is −1580 cm^3 mol^{-1} at 120 °C. Compare its compressibility factor at this temperature with that of a perfect gas at 1 bar.

SOLUTION

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} = 1 + \frac{BP}{RT}$$

In the B/V term, V may be replaced by RT/P if $Z \approx 1$, since the approximation is made in a small correction term. At 1 bar

$$Z = 1 + \frac{(-1.58\ \mathrm{L\ mol^{-1}})(1\ \mathrm{bar})}{(0.08314\ \mathrm{L\ bar\ K^{-1}\ mol^{-1}})(393.15\ \mathrm{K})}$$

$$= 0.952$$

The compressibility factor for a perfect gas is of course unity.

1.4 Using Fig. 1.4 calculate the compressibility factor Z for $NH_3(g)$ at 400 K and 50 bar.

SOLUTION $B = -110\ \mathrm{cm^3\ mol^{-1}}$

$$B' = \frac{B}{RT} = \frac{-(110\ \mathrm{cm^3\ mol^{-1}})(10^{-3}\ \mathrm{L\ cm^{-3}})}{(0.08314\ \mathrm{L\ bar\ K^{-1}\ mol^{-1}})(400\ \mathrm{K})}$$

$$= -3.31 \times 10^{-3}\ \mathrm{bar^{-1}}$$

$$Z = 1 + B'P = 1 - (3.31 \times 10^{-3}\ \mathrm{bar^{-1}})(50\ \mathrm{bar})$$

$$= 0.835$$

1.5 Derive the expressions for van der Waals constants a and b in terms of the critical temperature and pressure; that is, derive equations 1.35 and 1.36 from 1.32 - 1.34.

SOLUTION

Equations 1.32 and 1.33 may be written

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^{\,3}} \qquad (1)$$

$$\frac{2RT_c}{(V_c - b)^3} = \frac{6a}{V_c^{\,4}} \qquad (2)$$

Division of the first equation by the second yields

$$V_c = 3b \qquad (3)$$

Substitution of this expression in equation 1 yields

$$T_c = 8a/27Rb \qquad (4)$$

Substitution of equations 3 and 4 in equation 1.34 yields

$$P_c = a/27b^2 \qquad (5)$$

Since there are three relations (equations 3 - 5) between the van der Waals constants and the critical constants, a and b may be expressed in terms of T_c and P_c or T_c and V_c. Critical pressures are generally known more accurately than critical volumes, and so a and b are generally calculated using equations 1.35 and 1.36.

1.6 Calculate the second virial coefficient of methane at 400 K and 300 K from its van der Waals constants, and compare these results with Fig. 1.4.

SOLUTION

For methane a = 2.283 L^2 bar mol^{-2} and b = 0.04278 L mol^{-1}. From equation 1.28, the virial coefficient at 400 K is

$$B = b - a/RT = 0.04278 - 2.283/(0.083144)(400)$$
$$= -0.026 \text{ L mol}^{-1}$$

compared with -0.020 L mol^{-1} from Fig. 1.4. The calculated virial coefficient at 300 K is -0.048 L mol, compared with 0.050 L mol^{-1} in Fig. 1.4.

1.7 The critical temperature of carbon tetrachloride is 283.1 °C. The densities in grams per cubic centimeter of the liquid ρ_l and vapor ρ_v at different temperatures are as follows:

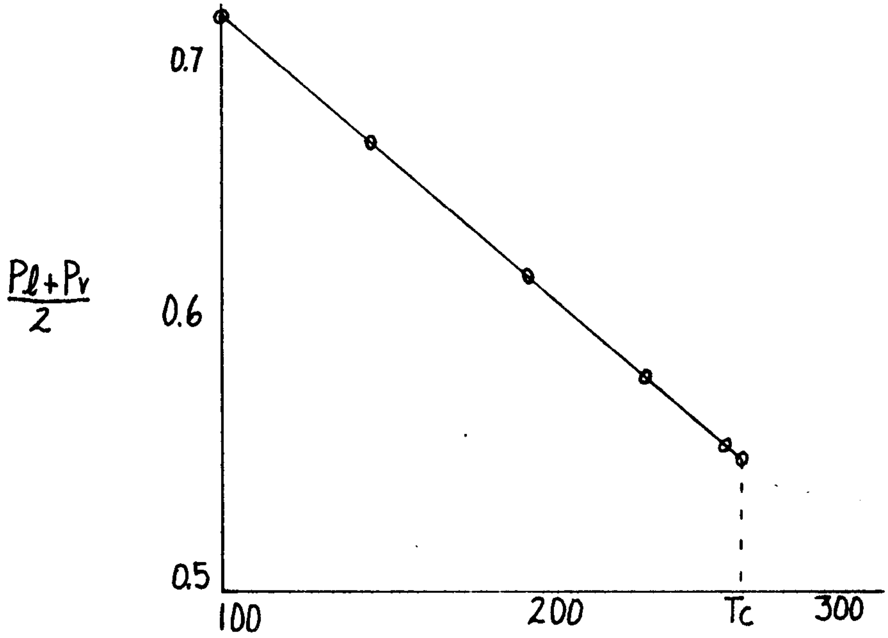
$t/°C$	100	150	200	250	270	280
ρ_l	1.4343	1.3215	1.1888	0.9980	0.8666	0.7634
ρ_v	0.0103	0.0304	0.0742	0.1754	0.2710	0.3597

What is the critical molar volume of CCl_4? It is found that the mean of the densities of the liquid and vapor does not vary rapidly with temperature and can be represented by

$$\frac{\rho_l + \rho_v}{2} = AT + B$$ where A and B are constants.

The extrapolated value of the average density at the critical temperature is the critical density. The molar volume V_c at the critical point is equal to the molar mass divided by the critical density.

SOLUTION



Extrapolating $\frac{\rho_1 + \rho_v}{2}$ to T_c we obtain

$\rho_c = 0.557 \text{ g cm}^{-3}$

$$V_c = \frac{153.84 \text{ g mol}^{-1}}{0.557 \text{ g cm}^{-3}} = 276 \text{ cm}^3 \text{ mol}^{-1}$$

1.8 Use the van der Waals constants for H_2 and O_2 in Table 1.3 to calculate the initial slopes of the plots of the compressibility factor Z versus P.

SOLUTION

$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right) P + \ldots$$

At 273.15 K, $RT = (0.083144 \text{ L bar K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})$

$= 22.71 \text{ L bar mol}^{-1}$

For H_2, $Z = 1 + (22.71)^{-1} [0.0266 - (0.2476/22.71)] P + \ldots$

$= 1 + (6.92 \times 10^{-4} \text{ bar}^{-1}) P + \ldots$

For O_2, $Z = 1 + (22.71)^{-1} [0.0318 - (1.378/22.71)] P + \ldots$

$= 1 - (4.07 \times 10^{-3} \text{ bar}) P + \ldots$

See Fig. 1.2

1.9 A mole of ethane is contained in a 200 ml-cylinder at 373 K. What is the pressure according to (a) the perfect gas law and (b) the van der Waals equation? The van der Waals constants are given in Table 1.3.

SOLUTION

(a) $P = RT/V = (.08314)(373)/0.200 = 155 \text{ bar}$

(b) $$P = \frac{RT}{V - b} - \frac{a}{V^2} = \frac{(0.08314)(373)}{0.200 - 0.0638} - \frac{5.562}{(0.200)^2}$$

$= 88.6 \text{ bar}$

1.10 What is the molar volume of n-hexane at 660 K and 91 bar according to (a) the perfect gas law, (b) the van der Waals equation, and (c) the Redlich-Kwong equation? $T_c = 507.7$ K $P_c = 30.3$ bar

SOLUTION

(a) $$V = \frac{RT}{P} = \frac{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(660 \text{ K})}{91 \text{ bar}} = 0.603 \text{ L mol}^{-1}$$

(b) $$a = \frac{27\ R^2\ T_c^{\ 2}}{64\ P_c} = \frac{(27)(0.08314)^2(507.7)^2}{(64)(30.3)}$$

$$= 24.81\ L^2\ bar\ mol^{-2}$$

$$b = \frac{RT_c}{8\ P_c} = \frac{(0.08314)(507.7)}{8(30.3)}$$

$$= 0.174\ L\ mol^{-1}$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$91\ bar = \frac{(0.08314)(660\ K)}{V - 0.174} - \frac{24.81}{V^2}$$

Rather than solving a cubic equation, substituting successive values of V shows that

$$V = 0.39\ L\ mol^{-1}.$$

(c) $$a = 0.4275\ R^2\ T_c^{\ 2.5}/P_c = 0.4275(.08314)^2(507.7)^{2.5}/30.3$$

$$= 566.4\ L^2\ bar\ K^{1/2}\ mol^{-2}$$

$$b = 0.0866\ RT_c/P_c = (0.0866)(.08314)(507.7)/30.3$$

$$= 0.121\ L\ mol^{-1}$$

$$P = \frac{RT}{V - b} - \frac{a}{T^{1/2}\ V(V + b)}$$

$$= \frac{(.08314)(660)}{V - 0.121} - \frac{566.4}{(660)^{1/2}\ V(V + 0.121)}$$

Trying successive values of V shows that $V = 0.40\ L\ mol^{-1}$.

1.11 Derive equation 1.25 that gives the boundary of the physically unrealizable region for a van der Waals gas and show that the maximum pressure satisfying this equation is the critical pressure.

SOLUTION $$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

Eliminating RT between these equations yields

$$P = \frac{a}{V^2}\left(1 - \frac{2b}{V}\right)$$

The maximum pressure according to this equation is obtained by differentiating with respect to V.

$$\frac{dP}{dV} = 0 = -\frac{2a}{V^3} + \frac{6ab}{V^4} \quad \text{so that} \quad b = \frac{V_c}{3} = \frac{RT_c}{8P_c}$$ where equation 1.37 has been used.

1.12 When pressure is applied to a liquid, its volume decreases. Assuming that the isothermal compressibility $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ is independent of pressure, derive an expression for the volume as a function of pressure.

SOLUTION

$$\int_{V_1}^{V_2} \frac{dV}{V} = -\kappa \int_{P_1}^{P_2} dP$$

$$\ln \frac{V_2}{V_1} = -\kappa (P_2 - P_1)$$

$$V_2 = V_1\, e^{-\kappa(P_2 - P_1)}$$

1.13 The coefficient of cubic expansion coefficient α is defined by $\alpha = \left(\frac{1}{V}\,\frac{\partial V}{\partial T}\right)_P$ and the isothermal compressibility is defined by $\kappa = \left(\frac{1}{V}\,\frac{\partial V}{\partial P}\right)_T$ Calculate these quantities for a perfect gas.

SOLUTION

$$V = RT/P$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$\alpha = 1/T$$

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{RT}{P^2}$$

$$\kappa = \frac{RT}{VP^2} = 1/P$$

1.14 Assuming that the atmosphere is isothermal at 0 °C and that the average molar mass of air is 29 g mol^{-1}, calculate the atmospheric pressure at 20,000 ft above sea level.

SOLUTION

$h = (2.0 \times 10^4 \text{ ft})(12 \text{ in ft}^{-1})(2.54 \text{ cm in}^{-1})(10^{-2} \text{ m cm}^{-1}) = 6096 \text{ m}$

$P = P_o e^{-gMh/RT}$

$$P = (1.013 \text{ bar}) \exp\left[\frac{-(9.8 \text{ m s}^{-2})(29 \times 10^{-3} \text{ kg mol}^{-1})(6096 \text{ m})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(273 \text{ K})}\right]$$

$= 0.472 \text{ bar}$

1.15 Calculate the pressure and composition of air on the top of Mt. Everest assuming the atmosphere has a temperature of 0 °C independent of altitude (h = 29,141 ft).

SOLUTION

$h = (29{,}141 \text{ ft})(12 \text{ in ft}^{-1})(2.54 \text{ cm in}^{-1})(0.01 \text{ m cm}^{-1}) = 8{,}882 \text{ m}$

For O_2, $P = (0.2 \text{ bar}) \exp(-9.8 \times 32 \times 10^{-3} \times 8882/8.314 \times 273)$
$= 0.059 \text{ bar}$

For N_2, $P = (0.8 \text{ bar}) \exp(-9.8 \times 28 \times 10^{-3} \times 8882/8.314 \times 273)$
$= 0.274 \text{ bar}$

The total pressure is 0.333 bar, and $y_{O_2} = 0.177$ and $y_{N_2} = 0.823$.

1.16 $B = -K_c$

1.17 21.7 cm^3 mol^{-1}

1.18 275.9 $cm^3\ mol^{-1}$

1.19 $\kappa = 0.28$

1.20 $T_c \approx 435$ K (actual 425 K)
$V_c = 0.261$ L mol^{-1} (actual 0.255 L mol^{-1})
$P_c = 39$ bar (actual 38.0 bar)

1.22 0.324 nm

1.23 -1.96×10^{-3} and -0.60×10^{-4} bar^{-1}

1.24 (a) 19.8 (b) 1621 (c) 2739 bar

1.25 (a) 100 (b) 152 bar

1.26 $\alpha = 1/T(1 + bP/RT)$ $\kappa = 1/P(1 + bP/RT)$

1.27 $V = V_o \exp[\alpha(T - T_o)]$
$V = V_o [1 + \alpha(T - T_o)]$

1.28 0.843 bar

1.29 3.27×10^{-9} bar $y_{O_2} = 0.015$ $y_{N_2} = 0.985$

CHAPTER 2: First Law of Thermodynamics

2.1 How much work is done when a person weighing 75 kg (165 lbs) climbs the Washington monument, 555 ft high? How many kilojoules must be supplied to do this muscular work, assuming that 25% of the energy produced by the oxidation of food in the body can be converted into muscular mechanical work?

SOLUTION

$w = mgh$

work = (mass)(acceleration of gravity)(height)

$= (75\ \mathrm{kg})(9.806\ \mathrm{m\ s^{-2}})(555\ \mathrm{ft})(12\ \mathrm{in\ ft^{-1}})$

$(2.54 \times 10^{-2}\ \mathrm{m\ in^{-1}})$

$= 124.4\ \mathrm{kJ}$

The energy needed is four times greater than the work done.

$E = 4(124.4\ \mathrm{kJ})$

$= 497.6\ \mathrm{kJ}$

2.2 The surface tension of water is $71.97 \times 10^{-3}\ \mathrm{N\ m^{-1}}$ or $71.97 \times 10^{-3}\ \mathrm{J\ m^{-2}}$ at 25 °C. Calculate the surface energy in joules of 1 mol of water dispersed as a mist containing droplets 1 μm (10^{-4} cm) in radius. The density of water may be taken as $1.00\ \mathrm{g\ cm^{-3}}$.

SOLUTION

The ratio of area to volume for a droplet is the same as the ratio of area to volume for the whole 18 cm^3.

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(10^{-6}\ \mathrm{m})^3$$

$$A = 4\pi r^2 = 4\pi(10^{-6}\ \mathrm{m})^2$$

$$\frac{\text{Total area}}{18 \times 10^{-6}\ \mathrm{m}^3} = \frac{4\pi(10^{-6}\ \mathrm{m})^2}{\frac{4}{3}\pi(10^{-6}\ \mathrm{m})^3} \qquad \text{Total area} = 54\ \mathrm{m}^2$$