



8TH EDITION

PHYSICAL CHEMISTRY

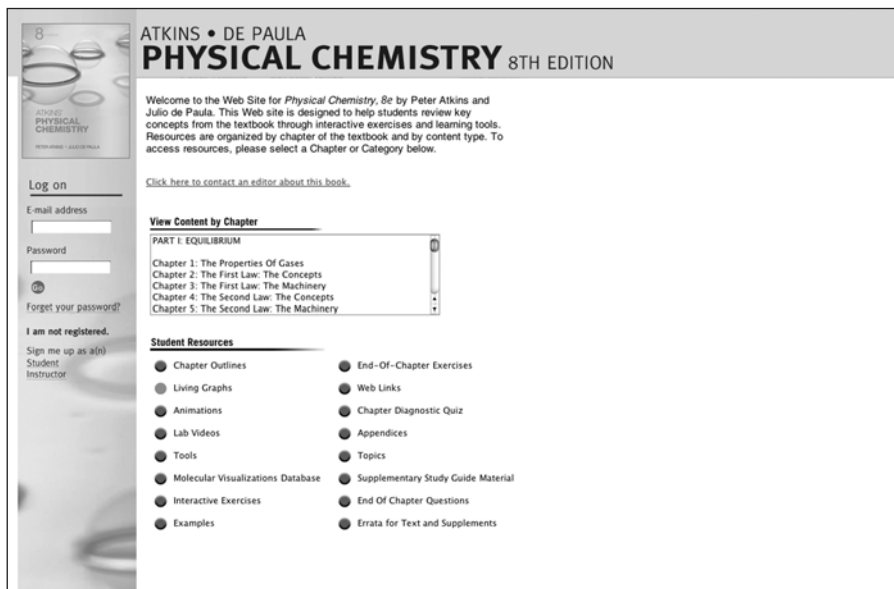
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ATKINS'
**PHYSICAL
CHEMISTRY**

About the Web site


The Web site to accompany *Physical Chemistry* is available at:

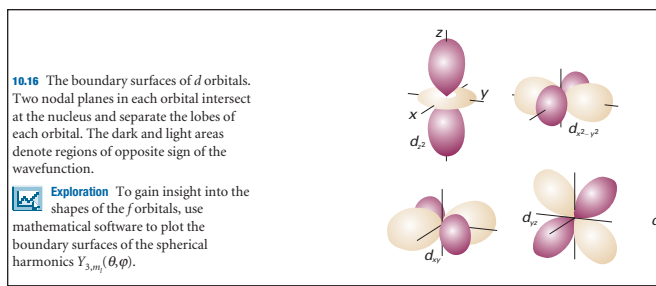
www.whfreeman.com/pchem8



It includes the following features:

Living graphs

A *Living graph* is indicated in the text by the icon  attached to a graph. This feature can be used to explore how a property changes as a variety of parameters are changed. To encourage the use of this resource (and the more extensive *Explorations in Physical Chemistry*) we have added a question to each figure where a *Living graph* is called out.



PART 1 Equilibrium

1 The properties of gases

Answers to discussion questions

- D1.2** The partial pressure of a gas in a mixture of gases is the pressure the gas would exert if it occupied alone the same container as the mixture at the same temperature. It is a limiting law because it holds exactly only under conditions where the gases have no effect upon each other. This can only be true in the limit of zero pressure where the molecules of the gas are very far apart. Hence, Dalton's law holds exactly only for a mixture of perfect gases; for real gases, the law is only an approximation.
- D1.4** The critical constants represent the state of a system at which the distinction between the liquid and vapor phases disappears. We usually describe this situation by saying that above the critical temperature the liquid phase cannot be produced by the application of pressure alone. The liquid and vapor phases can no longer coexist, though fluids in the so-called supercritical region have both liquid and vapor characteristics. (See *Impact* I.4.1 for a more thorough discussion of the supercritical state.)
- D1.6** The van der Waals equation is a cubic equation in the volume, V . Any cubic equation has certain properties, one of which is that there are some values of the coefficients of the variable where the number of real roots passes from three to one. In fact, any equation of state of odd degree higher than 1 can in principle account for critical behavior because for equations of odd degree in V there are necessarily some values of temperature and pressure for which the number of real roots of V passes from n (odd) to 1. That is, the multiple values of V converge from n to 1 as $T \rightarrow T_c$. This mathematical result is consistent with passing from a two phase region (more than one volume for a given T and p) to a one phase region (only one V for a given T and p and this corresponds to the observed experimental result as the critical point is reached.

Solutions to exercises

- E1.1(b)** (a) The perfect gas law is

$$pV = nRT$$

implying that the pressure would be

$$p = \frac{nRT}{V}$$

- (b) The Henry's law constants are determined by plotting the data and extrapolating the low concentration data to $x = 1$. The data are plotted in Figure 5.3. K_A and K_I are estimated as graphical tangents at $x_I = 1$ and $x_I = 0$, respectively. The values obtained are: $K_A = 60.0 \text{ kPa}$ and $K_I = 62.0 \text{ kPa}$

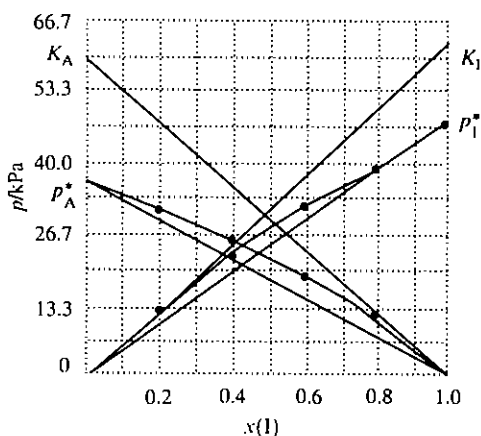


Figure 5.3

Then draw up the following table based on the values of the partial pressures obtained from the plots at the values of x_I given in the figure.

x_I	0	0.2	0.4	0.6	0.8	1.0
p_I/kPa	0	12.3	22.0	30.7	38.7	47.12^\ddagger
p_A/kPa	37.38^\ddagger	30.7	24.7	18.0	10.7	0
$\gamma_I(\text{R})$	—	1.30	1.17	1.09	1.03	$1.000[p_I/x_I p_I^*]$
$\gamma_A(\text{R})$	1.000	1.03	1.10	1.20	1.43	$— [p_A/x_A p_A^*]$
$\gamma_I(\text{H})$	1.000	0.990	0.887	0.824	0.780	$0.760[p_I/x_I K_I^*]$

‡ The value of p_A^* ; ‡ the value of p_I^* .

Question. In this problem both I and A were treated as solvents, but only I as a solute. Extend the table by including a row for $\gamma_A(\text{H})$.

P5.10 The partial molar volume of cyclohexane is

$$V_c = \left(\frac{\partial V}{\partial n_c} \right)_{p, T, n_2}$$

A similar expression holds for V_p . V_c can be evaluated graphically by plotting V against n_c and finding the slope at the desired point. In a similar manner, V_p can be evaluated by plotting V against n_p . To find V_c , V is needed at a variety of n_c while holding n_p constant, say at 1.0000 mol; likewise to find V_p , V is needed at a variety of n_p while holding n_c constant. The mole fraction in this system is

$$x_c = \frac{n_c}{n_c + n_p} \quad \text{so } n_c = \frac{x_c n_p}{1 - x_c}$$

From n_c and n_p , the mass of the sample can be calculated, and the volume can be calculated from

$$V = \frac{m}{\rho} = \frac{n_c M_c + n_p M_p}{\rho}$$

where the minus sign indicates flow toward lower temperature and

$$\lambda = \frac{1}{\sqrt{2}N\sigma}, \quad \bar{c} = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}, \quad \text{and } [M] = n/V = N/N_A$$

$$\begin{aligned} \text{So } J &= -\frac{2C_{V,m}}{3\sigma N_A} \left(\frac{RT}{\pi M}\right)^{1/2} \frac{dT}{dz} \\ &= \left(\frac{2 \times (28.832 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}}{3 \times [0.27 \times (10^{-9} \text{ m})^2] \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right) \\ &\quad \times \left(\frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (260 \text{ K})}{\pi \times (2.016 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \times (3.5 \text{ K m}^{-1}) \\ &= \boxed{0.17 \text{ J m}^{-2} \text{ s}^{-1}} \end{aligned}$$

E21.13(b) The thermal conductivity is

$$\begin{aligned} \kappa &= \frac{1}{3} \lambda C_{V,m} \bar{c} [X] = \frac{2C_{V,m}}{3\sigma N_A} \left(\frac{RT}{\pi M}\right)^{1/2} \quad \text{so } \sigma = \frac{2C_{V,m}}{3\kappa N_A} \left(\frac{RT}{\pi M}\right)^{1/2} \\ \kappa &= (0.240 \text{ mJ cm}^{-2} \text{ s}^{-1}) \times (\text{K cm}^{-1})^{-1} = 0.240 \times 10^{-1} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1} \\ \text{so } \sigma &= \left(\frac{2 \times (29.125 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}}{3 \times (0.240 \times 10^{-1} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}) \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right) \\ &\quad \times \left(\frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{\pi \times (28.013 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \\ &= \boxed{1.61 \times 10^{-19} \text{ m}^2} \end{aligned}$$

E21.14(b) Assuming the space between sheets is filled with air, the flux is

$$\begin{aligned} J &= -k \frac{dT}{dz} = \left[(0.241 \times 10^{-3} \text{ J cm}^{-2} \text{ s}^{-1}) \times (\text{K cm}^{-1})^{-1} \right] \times \left(\frac{[50 - (-10) \text{ K}]}{10.0 \text{ cm}} \right) \\ &= 1.45 \times 10^{-3} \text{ J cm}^{-2} \text{ s}^{-1}. \end{aligned}$$

So the rate of energy transfer and energy loss is

$$JA = (1.45 \times 10^{-3} \text{ J cm}^{-2} \text{ s}^{-1}) \times (1.50 \text{ m}^2) \times (100 \text{ cm m}^{-1})^2 = \boxed{22 \text{ J s}^{-1}}$$

E21.15(b) The coefficient of viscosity is

$$\begin{aligned} \eta &= \frac{1}{3} \lambda m N \bar{c} = \frac{2}{3\sigma} \left(\frac{mkT}{\pi}\right)^{1/2} \quad \text{so } \sigma = \frac{2}{3\eta} \left(\frac{mkT}{\pi}\right)^{1/2} \\ \eta &= 1.66 \mu\text{P} = 166 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1} \end{aligned}$$