

OXFORD



INSTRUCTOR'S SOLUTIONS
MANUAL TO ACCOMPANY

Atkins'
**Physical
Chemistry**

NINTH EDITION

CHARLES TRAPP ■ MARSHALL CADY ■ CARMEN GIUNTA

Contents

Fundamentals	1	Solutions to exercises	59
Exercises	1	Solutions to problems	66
F.1 Atoms	1	Solutions to numerical problems	66
F.2 Molecules	2	Solutions to theoretical problems	73
F.3 Bulk matter	5	Solutions to applications	80
F.4 Energy	6		
F.5 The relationship between molecular and bulk properties	8	4 Physical transformations of pure substances	84
F.6 The electromagnetic field	9		
F.7 Units	10	Answers to discussion questions	84
PART 1 Equilibrium	11	Solutions to exercises	85
1 The properties of gases	13	Solutions to problems	90
		Solutions to numerical problems	90
Answers to discussion questions	13	Solutions to theoretical problems	94
Solutions to exercises	13	Solutions to applications	96
Solutions to problems	23	5 Simple mixtures	99
Solutions to numerical problems	23		
Solutions to theoretical problems	26	Answers to discussion questions	99
Solutions to applications	30	Solutions to exercises	99
2 The first law	32	Solutions to problems	115
		Solutions to numerical problems	115
Answers to discussion questions	32	Solutions to theoretical problems	126
Solutions to exercises	32	Solutions to applications	128
Solutions to problems	43	6 Chemical equilibrium	133
Solutions to numerical problems	43		
Solutions to theoretical problems	49	Answers to discussion questions	133
Solutions to applications	54	Solutions to exercises	135
3 The second law	57	Solutions to problems	147
		Solutions to numerical problems	147
Answers to discussion questions	57	Solutions to theoretical problems	155
		Solutions to applications: biology, environmental science, and chemical engineering	157

PART 2 Structure	163	Answers to discussion questions	267
7 Quantum theory: introduction and principles	165	Solutions to exercises	268
Answers to discussion questions	165	Solutions to problems	275
Solutions to exercises	166	Solutions to numerical problems	275
Solutions to problems	171	Solutions to applications: astrophysics and biology	280
Solutions to numerical problems	171	12 Molecular spectroscopy 1: rotational and vibrational spectra	284
Solutions to theoretical problems	174	Answers to discussion questions	284
Solutions to applications: nanoscience, environmental science, and astrophysics	183	Solutions to exercises	285
8 Quantum theory: techniques and applications	189	Solutions to problems	295
Answers to discussion questions	189	Solutions to numerical problems	295
Solutions to exercises	190	Solutions to theoretical problems	300
Solutions to problems	199	Solutions to applications	302
Solutions to numerical problems	199	13 Molecular spectroscopy 2: electronic transitions	306
Solutions to theoretical problems	202	Answers to discussion questions	306
Solutions to applications	211	Solutions to exercises	307
9 Atomic structure and atomic spectra	215	Solutions to problems	317
Answers to discussion questions	215	Solutions to numerical problems	317
Solutions to exercises	216	Solutions to theoretical problems	322
Solutions to problems	226	Solutions to applications: biochemistry, environmental science, and astrophysics	324
Solutions to numerical problems	226	14 Molecular spectroscopy 3: magnetic resonance	329
Solutions to theoretical problems	230	Answers to discussion questions	329
Solutions to applications	235	Solutions to exercises	331
10 Molecular structure	240	Solutions to problems	338
Answers to discussion questions	240	Solutions to numerical problems	338
Solutions to exercises	241	Solutions to theoretical problems	343
Solutions to problems	249	Solutions to applications	344
Solutions to numerical problems	249	15 Statistical thermodynamics 1: the concepts	348
Solutions to theoretical problems	257	Answers to discussion questions	348
Solutions to applications	262	Solutions to exercises	349
11 Molecular symmetry	267		

viii CONTENTS

Solutions to problems	361	PART 3 Change	467
Solutions to numerical problems	361		
Solutions to theoretical problems	363	20 Molecules in motion	469
Solutions to applications	368		
16 Statistical thermodynamics 2: applications	371	Answers to discussion questions	469
		Solutions to exercises	470
Answers to discussion questions	371	Solutions to problems	484
Solutions to exercises	372	Solutions to numerical problems	484
Solutions to problems	380	Solutions to theoretical problems	489
Solutions to numerical problems	380	Solutions to applications: astrophysics and biochemistry	492
Solutions to theoretical problems	385		
Solutions to applications	394	21 The rates of chemical reactions	496
17 Molecular interactions	398		
		Answers to discussion questions	496
Answers to discussion questions	398	Solutions to exercises	498
Solutions to exercises	400	Solutions to problems	506
Solutions to problems	404	Solutions to numerical problems	506
Solutions to numerical problems	404	Solutions to theoretical problems	515
Solutions to theoretical problems	408	Solutions to applications	520
Solutions to applications: biochemistry	410	22 Reaction dynamics	522
18 Materials 1: macromolecules and self-assembly	413		
		Answers to discussion questions	522
Answers to discussion questions	413	Solutions to exercises	523
Solutions to exercises	415	Solutions to problems	533
Solutions to problems	421	Solutions to numerical problems	533
Solutions to numerical problems	421	Solutions to theoretical problems	539
Solutions to theoretical problems	425	Solutions to applications	541
Solutions to applications: biochemistry and technology	430	23 Catalysis	544
19 Solids	437		
		Answers to discussion questions	544
Answers to discussion questions	437	Solutions to exercises	546
Solutions to exercises	439	Solutions to problems	550
Solutions to problems	449	Solutions to numerical problems	550
Solutions to numerical problems	449	Solutions to theoretical problems	558
Solutions to theoretical problems	454	Solutions to applications: chemical engineering and environmental science	560
Solutions to applications: biochemistry and nanoscience	464		

F5.3(b) The Maxwell distribution of speeds indicates that a few molecules have either very low or very high speeds. Furthermore, the distribution peaks at lower speeds when either the temperature is low or the molecular mass is high. The distribution peaks at high speeds when either the temperature is high or the molecular mass is low.

F5.4(b) Rates of chemical reaction typically increase with increasing temperature because more molecules have the requisite speed and corresponding kinetic energy to promote excitation and bond breakage during collision at the high temperatures.

F5.5(b) $v_{\text{mean}} \propto (T/M)^{1/2}$ [F.11]

$$\frac{v_{\text{mean}}(T_2)}{v_{\text{mean}}(T_1)} = \frac{(T_2/M)^{1/2}}{(T_1/M)^{1/2}} = \left(\frac{T_2}{T_1}\right)^{1/2}$$

$$\frac{v_{\text{mean}}(303 \text{ K})}{v_{\text{mean}}(293 \text{ K})} = \left(\frac{303 \text{ K}}{293 \text{ K}}\right)^{1/2} = \boxed{1.02}$$

F5.6(b) A gaseous helium atom has three translational degrees of freedom (the components of motion in the x , y , and z directions). Consequently, the equipartition theorem assigns a mean energy of $\frac{3}{2}kT$ to each atom. The molar internal energy, U_{m} , is

$$U_{\text{m}} = \frac{3}{2} N_{\text{A}} kT = \frac{3}{2} RT \text{ [F.10]} = \frac{3}{2} (8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(303 \text{ K}) = 3.78 \text{ kJ mol}^{-1}$$

$$U = n U_{\text{m}} = m M^{-1} U_{\text{m}} = (10.0 \text{ g}) \left(\frac{1 \text{ mol}}{4.00 \text{ g}} \right) \left(\frac{3.78 \text{ kJ}}{\text{mol}} \right) = \boxed{9.45 \text{ kJ}}$$

F5.7(b) A solid-state lead atom has three vibrational quadratic degrees of freedom (the components of vibrational motion in the x , y , and z directions). Its potential energy also has a quadratic form in each direction because $V \propto (x - x_{\text{eq}})^2$. There are a total of six quadratic degrees of freedom for the atom because the atoms have no translational or rotational motion. Consequently, the equipartition theorem assigns a mean energy of $\frac{6}{2}kT = 3kT$ to each atom. This is the **law of Dulong and Petit**. The molar internal energy, U_{m} , is

$$U_{\text{m}} = 3 N_{\text{A}} kT = 3RT \text{ [F.10]} = 3(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(293 \text{ K}) = 7.31 \text{ kJ mol}^{-1}$$

$$U = n U_{\text{m}} = m M^{-1} U_{\text{m}} = (10.0 \text{ g}) \left(\frac{1 \text{ mol}}{207.2 \text{ g}} \right) \left(\frac{7.31 \text{ kJ}}{\text{mol}} \right) = \boxed{0.353 \text{ kJ}}$$

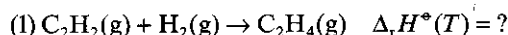
F.6 The electromagnetic field

F6.1(b) $\nu = \frac{c}{\lambda}$ [F.12] = $\frac{3.00 \times 10^8 \text{ m s}^{-1}}{720 \times 10^{-9} \text{ m}} = 4.17 \times 10^{14} \text{ s}^{-1} = \boxed{4.17 \times 10^{14} \text{ Hz}}$

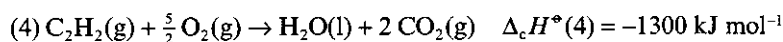
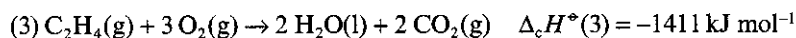
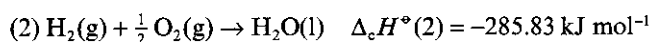
F6.2(b) $\tilde{\nu} = \frac{\nu}{c}$ [F.13] = $\frac{160 \times 10^6 \text{ s}^{-1}}{3.00 \times 10^8 \text{ m s}^{-1}} = \boxed{0.533 \text{ m}^{-1}}$

$$\begin{aligned}\Delta_r H^\circ(100^\circ\text{C}) &= [-571.66 + (373 - 298) \times (0.06606) + \frac{1}{2}(373^2 - 298^2) \\ &\quad \times (-10.76 \times 10^{-6}) - (67) \times (\frac{1}{373} - \frac{1}{298})] \text{ kJ mol}^{-1} \\ &= \boxed{-566.93 \text{ kJ mol}^{-1}}\end{aligned}$$

E2.27(b) The hydrogenation reaction is



The reactions and accompanying data which are to be combined in order to yield reaction (1) and $\Delta_r H^\circ(T)$ are



$$\text{reaction (1)} = \text{reaction (2)} - \text{reaction (3)} + \text{reaction (4)}$$

Hence, at 298 K:

$$\begin{aligned}(a) \quad \Delta_r H^\circ &= \Delta_c H^\circ(2) - \Delta_c H^\circ(3) + \Delta_c H^\circ(4) \\ &= [(-285.83) - (-1411) + (-1300)] \text{ kJ mol}^{-1} \\ &= \boxed{-175 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_r U^\circ &= \Delta_r H^\circ - \Delta n_g RT \quad [2.21]; \quad \Delta n_g = -1 \\ &= -175 \text{ kJ mol}^{-1} - (-1) \times (2.48 \text{ kJ mol}^{-1}) \\ &= \boxed{-173 \text{ kJ mol}^{-1}}\end{aligned}$$

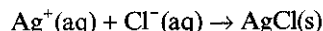
(b) At 348 K:

$$\Delta_r H^\circ(348 \text{ K}) = \Delta_r H^\circ(298 \text{ K}) + \Delta_r C_p^\circ(348 \text{ K} - 298 \text{ K}) \quad [\text{Example 2.6}]$$

$$\begin{aligned}\Delta_r C_p^\circ &= \sum_j \nu_j C_{p,m}^\circ(\text{J}) \quad [2.36b] = C_{p,m}^\circ(\text{C}_2\text{H}_4, \text{g}) - C_{p,m}^\circ(\text{C}_2\text{H}_2, \text{g}) - C_{p,m}^\circ(\text{H}_2, \text{g}) \\ &= (43.56 - 43.93 - 28.82) \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \\ &= -29.19 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_r H^\circ(348 \text{ K}) &= (-175 \text{ kJ mol}^{-1}) - (29.19 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (50 \text{ K}) \\ &= \boxed{-176 \text{ kJ mol}^{-1}}\end{aligned}$$

E2.28(b) NaCl, AgNO₃, and NaNO₃ are strong electrolytes, therefore the net ionic equation is



$$\begin{aligned}\Delta_r H^\circ &= \Delta_r H^\circ(\text{AgCl}) - \Delta_r H^\circ(\text{Ag}^+) - \Delta_r H^\circ(\text{Cl}^-) \\ &= [(-127.07) - (105.58) - (-167.16)] \text{ kJ mol}^{-1} \\ &= \boxed{-65.49 \text{ kJ mol}^{-1}}\end{aligned}$$

P2.24

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$\left(\frac{\partial C_V}{\partial V} \right)_T = \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T} \right)_V \right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T \right)_V \quad (\text{derivatives may be taken in any order})$$

$$\left(\frac{\partial U}{\partial V} \right)_T = 0 \text{ for a perfect gas [Section 2.11(b)]}$$

Hence, $\left(\frac{\partial C_V}{\partial V} \right)_T = 0$

Likewise $C_p = \left(\frac{\partial H}{\partial T} \right)_p$, so $\left(\frac{\partial C_p}{\partial p} \right)_T = \left(\frac{\partial}{\partial p} \left(\frac{\partial H}{\partial T} \right)_p \right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial p} \right)_T \right)_p$

$$\left(\frac{\partial H}{\partial p} \right)_T = 0 \text{ for a perfect gas.}$$

Hence, $\left(\frac{\partial C_p}{\partial p} \right)_T = 0$.

P2.26 Using Euler's chain relationship and the reciprocal identity [MB2.3c]

$$\left(\frac{\partial p}{\partial T} \right)_V = - \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p$$

Substituting into the given expression for $C_p - C_V$

$$C_p - C_V = -T \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p^2$$

Using the reciprocal identity again

$$C_p - C_V = - \frac{T \left(\frac{\partial V}{\partial T} \right)_p^2}{\left(\frac{\partial V}{\partial p} \right)_T}$$

For a perfect gas, $pV = nRT$, so

$$\left(\frac{\partial V}{\partial T} \right)_p = \left(\frac{nR}{p} \right) \quad \text{and} \quad \left(\frac{\partial V}{\partial p} \right)_T = - \frac{nRT}{p^2}$$

$$\text{so } C_p - C_V = \frac{-T \left(\frac{nR}{p} \right)^2}{-\frac{nRT}{p^2}} = \boxed{nR}$$

P3.12

$$\Delta_r H^\circ = \sum_{\text{products}} \nu \Delta_f H^\circ - \sum_{\text{reactants}} \nu \Delta_f H^\circ \quad [2.34a]$$

$$\begin{aligned} \Delta_r H^\circ(298 \text{ K}) &= 1 \times \Delta_f H^\circ(\text{CO}_2, \text{g}) + 1 \times \Delta_f H^\circ(\text{H}_2\text{O}, \text{g}) - 1 \times \Delta_f H^\circ(\text{CO}, \text{g}) \\ &= \{-110.53 - 241.82 - (-393.51)\} \text{ kJ mol}^{-1} = \boxed{+41.16 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\Delta_r S^\circ = \sum_{\text{products}} \nu S_m^\circ - \sum_{\text{reactants}} \nu S_m^\circ \quad [3.25a]$$

$$\begin{aligned} \Delta_r S^\circ(298 \text{ K}) &= 1 \times S_m^\circ(\text{CO}_2, \text{g}) + 1 \times S_m^\circ(\text{H}_2\text{O}, \text{g}) - 1 \times S_m^\circ(\text{CO}, \text{g}) - 1 \times S_m^\circ(\text{H}_2, \text{g}) \\ &= (197.67 + 188.83 - 213.74 - 130.684) \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{+42.08 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} \Delta_r H^\circ(398 \text{ K}) &= \Delta_r H^\circ(298 \text{ K}) + \int_{298 \text{ K}}^{398 \text{ K}} \Delta_r C_p^\circ dT \quad [2.36a] \\ &= \Delta_r H^\circ(298 \text{ K}) + \Delta_r C_p^\circ \Delta T \quad [\text{heat capacities constant}] \end{aligned}$$

$$\begin{aligned} \Delta_r C_p^\circ &= 1 \times C_{p,m}^\circ(\text{CO}_2, \text{g}) + 1 \times C_{p,m}^\circ(\text{H}_2\text{O}, \text{g}) - 1 \times C_{p,m}^\circ(\text{CO}, \text{g}) - 1 \times C_{p,m}^\circ(\text{H}_2, \text{g}) \\ &= (29.14 + 33.58 - 37.11 - 28.824) \text{ J K}^{-1} \text{ mol}^{-1} = -3.21 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\Delta_r H^\circ(398 \text{ K}) = (41.16 \text{ kJ mol}^{-1}) + (-3.21 \text{ J K}^{-1} \text{ mol}^{-1}) \times (100 \text{ K}) = \boxed{+40.84 \text{ kJ mol}^{-1}}$$

For each substance in the reaction

$$\Delta S_m = C_{p,m} \ln \left(\frac{T_f}{T_i} \right) = C_{p,m} \ln \left(\frac{398 \text{ K}}{298 \text{ K}} \right) \quad [3.23]$$

Thus,

$$\begin{aligned} \Delta_r S^\circ(398 \text{ K}) &= \Delta_r S^\circ(298 \text{ K}) + \sum_{\text{products}} \nu C_{p,m}^\circ \ln \left(\frac{T_f}{T_i} \right) - \sum_{\text{reactants}} \nu C_{p,m}^\circ \ln \left(\frac{T_f}{T_i} \right) \\ &= \Delta_r S^\circ(298 \text{ K}) + \Delta_r C_p^\circ \ln \left(\frac{398 \text{ K}}{298 \text{ K}} \right) \\ &= (42.08 \text{ J K}^{-1} \text{ mol}^{-1}) + (-3.21 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left(\frac{398 \text{ K}}{298 \text{ K}} \right) \\ &= (42.08 - 0.93) \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{+41.15 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

COMMENT. Both $\Delta_r H^\circ$ and $\Delta_r S^\circ$ changed little over 100 K for this reaction. This is not an uncommon result.

P3.14

Draw up the following table and proceed as in Problem 3.11.

T/K	14.14	16.33	20.03	31.15	44.08	64.81
$(C_{p,m}/T)(\text{J K}^{-2} \text{ mol}^{-1})$	0.671	0.778	0.908	1.045	1.063	1.024

T/K	100.90	140.86	183.59	225.10	262.99	298.06
$(C_{p,m}/T)(\text{J K}^{-2} \text{ mol}^{-1})$	0.942	0.861	0.787	0.727	0.685	0.659

E4.17(b) $\Delta_{\text{vap}}H = \Delta_{\text{vap}}U + \Delta_{\text{vap}}(pV) = 43.5 \text{ kJ mol}^{-1}$

$$\Delta_{\text{vap}}(pV) = p\Delta_{\text{vap}}V = p(V_{\text{gas}} - V_{\text{liq}}) \approx pV_{\text{gas}} = RT \text{ [perfect gas]}$$

$$\Delta_{\text{vap}}(pV) \approx (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (352 \text{ K}) = 2.93 \times 10^3 \text{ J mol}^{-1}$$

$$\text{Fraction} = \frac{\Delta_{\text{vap}}(pV)}{\Delta_{\text{vap}}H} = \frac{2.93 \text{ kJ mol}^{-1}}{43.5 \text{ kJ mol}^{-1}} = \boxed{0.0673} = 6.73\%$$

Solutions to problems

Solutions to numerical problems

P4.2 Use the definite integral form of the Clausius–Clapeyron equation [Exercise 4.15(b)].

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta_{\text{vap}}H}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

At $T_1 = (273.15 - 29.2) \text{ K} = 244.0 \text{ K}$ (normal boiling point), $p_1 = 1.000 \text{ atm}$, thus, at 40°C

$$\ln\left(\frac{p_2}{1.000 \text{ atm}}\right) = \left(\frac{20.25 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{244.0 \text{ K}} - \frac{1}{313.2 \text{ K}}\right) = 2.205$$

and $p_2 = 1.000 \text{ atm} \times e^{2.205} = \boxed{9.07 \text{ atm}}$

COMMENT. Three significant figures are not really warranted in this answer because of the approximations employed.

P4.4

$$\begin{aligned} \text{(a)} \quad \left(\frac{\partial \mu(l)}{\partial T}\right)_p - \left(\frac{\partial \mu(s)}{\partial T}\right)_p &= -S_m(l) + S_m(s) = -\Delta_{\text{fus}}S = \frac{-\Delta_{\text{fus}}H}{T_f} \quad [4.13] \\ &= \frac{-6.01 \times 10^3 \text{ J mol}^{-1}}{273.15 \text{ K}} = \boxed{-22.0 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \left(\frac{\partial \mu(g)}{\partial T}\right)_p - \left(\frac{\partial \mu(l)}{\partial T}\right)_p &= -S_m(g) + S_m(l) = -\Delta_{\text{vap}}S = \frac{-\Delta_{\text{vap}}H}{T_b} \\ &= \frac{-40.6 \times 10^3 \text{ J mol}^{-1}}{373.15 \text{ K}} = \boxed{-108.8 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$\text{(c)} \quad \mu(l, -5^\circ\text{C}) - \mu(s, -5^\circ\text{C}) = \mu(l, -5^\circ\text{C}) - \mu(l, 0^\circ\text{C}) - \{\mu(s, -5^\circ\text{C}) - \mu(s, 0^\circ\text{C})\}$$

because $\mu(l, 0^\circ\text{C}) = \mu(s, 0^\circ\text{C})$

Thus, $\mu(l, -5^\circ\text{C}) - \mu(s, -5^\circ\text{C}) = \Delta\mu(l) - \Delta\mu(s)$

where $\Delta\mu$ is the difference in chemical potential of a given phase at -5°C compared to that at normal freezing temperature.

$$\Delta\mu \approx \left(\frac{\partial \mu}{\partial T}\right)_p \Delta T = -S_m \Delta T \quad [4.2],$$

For DBr

$$m_{\text{eff}}^{-1} = \frac{(2.0140 m_{\text{u}})^{-1} + (80.9163 m_{\text{u}})^{-1}}{1.66054 \times 10^{-27} \text{ kg } m_{\text{u}}^{-1}} = 3.0646 \times 10^{26} \text{ kg}^{-1}$$

$$\tilde{\nu} = \frac{\{(3.0646 \times 10^{26} \text{ kg}^{-1}) \times (411.75 \text{ kg s}^{-2})\}^{1/2}}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1})} = \boxed{1885.8 \text{ cm}^{-1}}$$

For DI

$$m_{\text{eff}}^{-1} = \frac{(2.0140 m_{\text{u}})^{-1} + (126.9045 m_{\text{u}})^{-1}}{1.66054 \times 10^{-27} \text{ kg } m_{\text{u}}^{-1}} = 3.0376 \times 10^{26} \text{ kg}^{-1}$$

$$\tilde{\nu} = \frac{\{(3.0376 \times 10^{26} \text{ kg}^{-1}) \times (314.21 \text{ kg s}^{-2})\}^{1/2}}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1})} = \boxed{1640.1 \text{ cm}^{-1}}$$

E12.19(b) Data on three transitions are provided. Only two are necessary to obtain the value of $\tilde{\nu}$ and x_e . The third datum can then be used to check the accuracy of the calculated values.

$$\Delta\tilde{G}(\nu = 1 \leftarrow 0) = \tilde{\nu} - 2\tilde{\nu}x_e = 2345.15 \text{ cm}^{-1} [12.40]$$

$$\Delta\tilde{G}(\nu = 2 \leftarrow 0) = 2\tilde{\nu} - 6\tilde{\nu}x_e = 4661.40 \text{ cm}^{-1} [12.41]$$

Multiply the first equation by 3, then subtract the second.

$$\tilde{\nu} = (3) \times (2345.15 \text{ cm}^{-1}) - (4661.40 \text{ cm}^{-1}) = \boxed{2374.05 \text{ cm}^{-1}}$$

Then, from the first equation

$$x_e = \frac{\tilde{\nu} - 2345.15 \text{ cm}^{-1}}{2\tilde{\nu}} = \frac{(2374.05 - 2345.15) \text{ cm}^{-1}}{(2) \times (2374.05 \text{ cm}^{-1})} = \boxed{6.087 \times 10^{-3}}$$

x_e data are usually reported as $x_e\tilde{\nu}$, which is

$$x_e\tilde{\nu} = 14.45 \text{ cm}^{-1}$$

$$\Delta\tilde{G}(\nu = 3 \leftarrow 0) = 3\tilde{\nu} - 12\nu x_e = (3) \times (2374.05 \text{ cm}^{-1}) - (12) \times (14.45 \text{ cm}^{-1}) = 6948.74 \text{ cm}^{-1}$$

which is close to the experimental value.

E12.20(b) $\Delta\tilde{G}_{\nu+1/2} = \tilde{\nu} - 2(\nu+1)x_e\tilde{\nu}$ [12.40], where $\Delta\tilde{G}_{\nu+1/2} = \tilde{G}(\nu+1) - \tilde{G}(\nu)$

Therefore, since

$$\Delta\tilde{G}_{\nu+1/2} = (1 - 2x_e)\tilde{\nu} - 2\nu x_e\tilde{\nu}$$

a plot of $\Delta\tilde{G}_{\nu+1/2}$ against ν should give a straight line, which gives $(1 - 2x_e)\tilde{\nu}$ from the intercept at $\nu = 0$ and $-2x_e\tilde{\nu}$ from the slope. We draw up the following table:

ν	0	1	2	3	4
$\tilde{G}(\nu)/\text{cm}^{-1}$	1144.83	3374.90	5525.51	7596.66	9588.35
$\tilde{G}_{\nu+1/2}/\text{cm}^{-1}$	2230.07	2150.61	2071.15	1991.69	

For a linear rotor, the degeneracies are $g(J) = 2J + 1$. The energies are

$$\epsilon(J) = hc\tilde{B}J(J+1) = \theta_R kJ(J+1)$$

$$\text{so } \beta\epsilon(J) = \theta_R J(J+1)/T$$

The total heat capacity and the contributions of several transitions are plotted in Figure 16.8. One can evaluate $C_{V,m}/R$ using the following expression, derivable from eqn (1) above. It has the advantage of using single sums rather than double sums.

$$\frac{C_{V,m}}{R} = \frac{1}{q} \sum_J g(J) \beta^2 \epsilon^2(J) e^{-\beta\epsilon(J)} - \frac{1}{q^2} \left(\sum_J g(J) \beta \epsilon(J) e^{-\beta\epsilon(J)} \right)^2$$

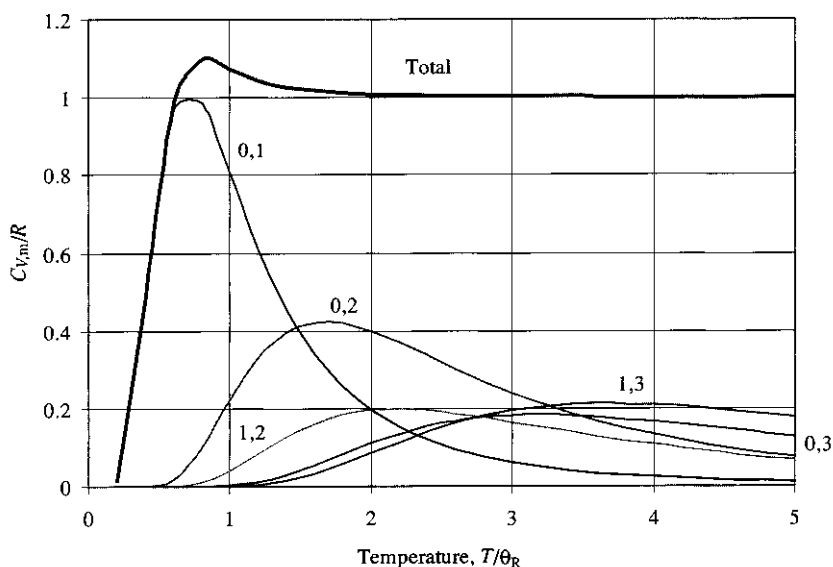


Figure 16.8

COMMENT. $\zeta(\beta)$ is defined in such a way that J and J' each run independently from 0 to infinity. Thus, identical terms appear twice. (For example, both (0,1) and (1,0) terms appear with identical values in $\zeta(\beta)$. In the plot, however, the (0,1) curve represents both terms.) One could redefine the double sum with an inner sum over J' running from 0 to $J - 1$ and an outer sum over J running from 0 to infinity. In that case, each term appears only once, and the overall factor of $\frac{1}{2}$ in C_V would have to be removed.

P16.22 Eqn 16.42 relates the second virial coefficient to the pairwise intermolecular potential energy:

$$B = -2\pi N_A \int_0^\infty f r^2 dr, \quad \text{where } f = e^{-\beta\epsilon_P} - 1$$

In order to relate the pairwise potential to the van der Waals equation, we must express that equation as a virial series. The equations are

$$\text{van der Waals } p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}; \quad \text{virial } p = \frac{RT}{V_m} \left(1 + \frac{B}{V_m} + \dots \right)$$

Solutions to applications: astrophysics and biochemistry

P20.30 Newton's gravitational force law: $F = \frac{Gmm'}{r^2}$, where G is the gravitational constant and r is the centre-to-centre distance between mass m and m' . In this problem $r \geq R$, where R is a planet radius. The minimum work w required to move an object of mass m from a position near the planet's surface to infinity is

$$w = \int_R^\infty F dr = Gmm' \int_R^\infty \frac{1}{r^2} dr = -Gmm' \times \left[\frac{1}{r} \right]_{r=R}^{r=\infty} = \left(\frac{Gm'}{R} \right) m = mg_{\text{planet}} R$$

where $g_{\text{planet}} = \frac{Gm'}{R^2}$ is the gravitational acceleration of a planet and $\frac{g_{\text{planet}}}{g_{\text{Earth}}} = \left(\frac{m}{R^2} \right)_{\text{planet}} / \left(\frac{m}{R^2} \right)_{\text{Earth}}$.

Using data provided in the problem:

$$\begin{aligned} g_{\text{Mars}} &= g_{\text{Earth}} \times \left(\frac{m}{R^2} \right)_{\text{Mars}} / \left(\frac{m}{R^2} \right)_{\text{Earth}} = g_{\text{Earth}} \times \left(\frac{m_{\text{Mars}}}{m_{\text{Earth}}} \right) \times \left(\frac{R_{\text{Earth}}}{R_{\text{Mars}}} \right)^2 \\ &= (9.81 \text{ m s}^{-2}) \times (0.108) \times \left(\frac{6.37}{3.38} \right)^2 = 3.76 \text{ m s}^{-2} \end{aligned}$$

The escape speed v_{esc} is determined by the minimum kinetic energy that provides the energy w .

$$\frac{1}{2} mv_{\text{esc}}^2 = (gR)_{\text{planet}} m, \quad \text{so that} \quad v_{\text{esc}} = (2gR)_{\text{planet}}^{1/2}$$

(a) The escape speed for Earth: $v_{\text{esc}} = [2 \times (9.81 \text{ m s}^{-2}) \times (6.37 \times 10^6 \text{ m})]^{1/2} = \boxed{11.2 \text{ km s}^{-1}}$

(b) The escape speed for Mars: $v_{\text{esc}} = [2 \times (3.76 \text{ m s}^{-2}) \times (3.38 \times 10^6 \text{ m})]^{1/2} = \boxed{5.04 \text{ km s}^{-1}}$

Since $\bar{c} = (8RT/\pi M)^{1/2}$ [20.7], the temperature at which the mean gas speed corresponds to the escape speed is given by $T = \pi M v_{\text{esc}}^2 / 8R$ and computed temperature values for hydrogen, helium, and oxygen are summarized in the following table:

$10^{-3} T/K$	H_2	He	O_2	
Earth	11.9	23.7	190	$[\bar{c} = 11.2 \text{ km s}^{-1}]$
Mars	2.4	4.8	38	$[\bar{c} = 5.0 \text{ km s}^{-1}]$

In order to calculate the proportion P of molecules that have speeds exceeding the escape velocity, we must integrate the Maxwell distribution [20.4] from v_{esc} to infinity. P is a function of M , T , and v_{esc} :

$$P(M, T, v_{\text{esc}}) = \int_{v_{\text{esc}}}^\infty f(v) dv = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \int_{v_{\text{esc}}}^\infty v^2 e^{-Mv^2/2RT} dv$$

The integral of this expression has no analytical solution but it is easily numerically performed on the scientific calculator or with computer software. Avoid unit errors by using SI units throughout. Here is a Mathcad setup for the computations along with the desired calculations: