

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
		Solutions to theoretical problems	94
		Solutions to applications	96
Answers to discussion questions	13		
Solutions to exercises	13	5 Simple mixtures	99
Solutions to problems	23		
Solutions to numerical problems	23	Answers to discussion questions	99
Solutions to theoretical problems	26	Solutions to exercises	99
Solutions to applications	30	Solutions to problems	115
		Solutions to numerical problems	115
2 The first law	32	Solutions to theoretical problems	126
		Solutions to applications	128
Answers to discussion questions	32		
Solutions to exercises	32	6 Chemical equilibrium	133
Solutions to problems	43		
Solutions to numerical problems	43	Answers to discussion questions	133
Solutions to theoretical problems	49	Solutions to exercises	135
Solutions to applications	54	Solutions to problems	147
		Solutions to numerical problems	147
3 The second law	57	Solutions to theoretical problems	155
		Solutions to applications: biology, environmental science, and chemical engineering	157
Answers to discussion questions	57		

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

viii CONTENTS

Solutions to problems	361
Solutions to numerical problems	361
Solutions to theoretical problems	363
Solutions to applications	368

16 Statistical thermodynamics 2: applications	371
--	------------

Answers to discussion questions	371
Solutions to exercises	372
Solutions to problems	380
Solutions to numerical problems	380
Solutions to theoretical problems	385
Solutions to applications	394

17 Molecular interactions	398
----------------------------------	------------

Answers to discussion questions	398
Solutions to exercises	400
Solutions to problems	404
Solutions to numerical problems	404
Solutions to theoretical problems	408
Solutions to applications: biochemistry	410

18 Materials 1: macromolecules and self-assembly	413
---	------------

Answers to discussion questions	413
Solutions to exercises	415
Solutions to problems	421
Solutions to numerical problems	421
Solutions to theoretical problems	425
Solutions to applications: biochemistry and technology	430

19 Solids	437
------------------	------------

Answers to discussion questions	437
Solutions to exercises	439
Solutions to problems	449
Solutions to numerical problems	449
Solutions to theoretical problems	454
Solutions to applications: biochemistry and nanoscience	464

PART 3 Change	467
----------------------	------------

20 Molecules in motion	469
-------------------------------	------------

Answers to discussion questions	469
Solutions to exercises	470
Solutions to problems	484
Solutions to numerical problems	484
Solutions to theoretical problems	489
Solutions to applications: astrophysics and biochemistry	492

21 The rates of chemical reactions	496
---	------------

Answers to discussion questions	496
Solutions to exercises	498
Solutions to problems	506
Solutions to numerical problems	506
Solutions to theoretical problems	515
Solutions to applications	520

22 Reaction dynamics	522
-----------------------------	------------

Answers to discussion questions	522
Solutions to exercises	523
Solutions to problems	533
Solutions to numerical problems	533
Solutions to theoretical problems	539
Solutions to applications	541

23 Catalysis	544
---------------------	------------

Answers to discussion questions	544
Solutions to exercises	546
Solutions to problems	550
Solutions to numerical problems	550
Solutions to theoretical problems	558
Solutions to applications: chemical engineering and environmental science	560

5.3(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.

5.4(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.

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

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

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

5.6(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

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

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

5.7(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

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

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

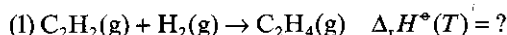
F.6 The electromagnetic field

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

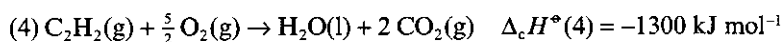
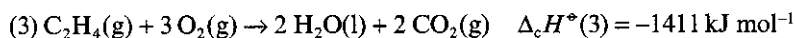
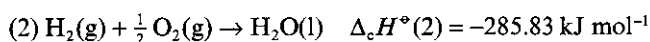
6.2(b) $\tilde{\nu} = \frac{\nu}{c}$ [F.13] = $\frac{160 \times 10^6 \text{ s}^{-1}}{3.00 \times 10^8 \text{ m s}^{-1}} = \boxed{0.533 \text{ m}^{-1}}$

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

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:

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

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

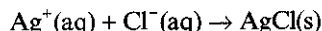
(b) At 348 K:

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

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

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

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



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

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

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

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

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 (a) $\left(\frac{\partial\mu(l)}{\partial T}\right)_p - \left(\frac{\partial\mu(s)}{\partial T}\right)_p = -S_m(l) + S_m(s) = -\Delta_{\text{fus}}S = \frac{-\Delta_{\text{fus}}H}{T_f}$ [4.13]

$$= \frac{-6.01 \times 10^3 \text{ J mol}^{-1}}{273.15 \text{ K}} = \boxed{-22.0 \text{ J K}^{-1} \text{ mol}^{-1}}$$

(b) $\left(\frac{\partial\mu(g)}{\partial T}\right)_p - \left(\frac{\partial\mu(l)}{\partial T}\right)_p = -S_m(g) + S_m(l) = -\Delta_{\text{vap}}S = \frac{-\Delta_{\text{vap}}H}{T_b}$

$$= \frac{-40.6 \times 10^3 \text{ J mol}^{-1}}{373.15 \text{ K}} = \boxed{-108.8 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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

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.

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

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.

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

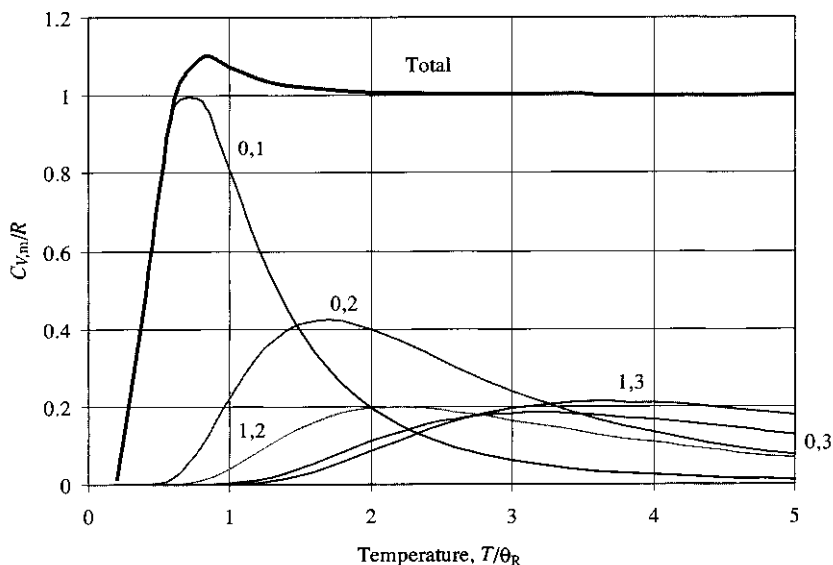


Figure 16.8

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: