OXFORD

INSTRUCTOR'S SOLUTIONS
MANUAL TO ACCOMPANY

Atkins'
Physical
Chemistry

NINTH EDITION

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Contents

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

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

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

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

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

$$U = nU_m = mM^{-1}U_m = (10.0\ g)\left(\frac{1\ mol}{4.00\ g}\right)\left(\frac{3.78\ kJ}{mol}\right) = \boxed{9.45\ kJ}$$

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 $V \propto (x - x_{eq})^2$. 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

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

$$U = nU_m = mM^{-1}U_m = (10.0\ g)\left(\frac{1\ mol}{207.2\ g}\right)\left(\frac{7.31\ kJ}{mol}\right) = \boxed{0.353\ kJ}$$

F.6 The electromagnetic field

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

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

$$\Delta_r H^{\ominus}(100°C) = [-571.66 + (373 - 298) \times (0.06606) + \tfrac{1}{2}(373^2 - 298^2)$$
$$\times (-10.76 \times 10^{-6}) - (67) \times (\tfrac{1}{373} - \tfrac{1}{298})] \text{ kJ mol}^{-1}$$
$$= \boxed{-566.93 \text{ kJ mol}^{-1}}$$

E2.27(b)   The hydrogenation reaction is

(1) $C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$ $\Delta_r H^{\ominus}(T) = ?$

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

(2) $H_2(g) + \tfrac{1}{2} O_2(g) \rightarrow H_2O(l)$ $\Delta_c H^{\ominus}(2) = -285.83 \text{ kJ mol}^{-1}$

(3) $C_2H_4(g) + 3 O_2(g) \rightarrow 2 H_2O(l) + 2 CO_2(g)$ $\Delta_c H^{\ominus}(3) = -1411 \text{ kJ mol}^{-1}$

(4) $C_2H_2(g) + \tfrac{5}{2} O_2(g) \rightarrow H_2O(l) + 2 CO_2(g)$ $\Delta_c H^{\ominus}(4) = -1300 \text{ kJ mol}^{-1}$

reaction (1) = reaction (2) – reaction (3) + reaction (4)

Hence, at 298 K:

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

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

(b)   At 348 K:

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

$$\Delta_r C_p^{\ominus} = \sum_J \nu_J C_{p,m}^{\ominus}(J) \text{ [2.36b]} = C_{p,m}^{\ominus}(C_2H_4, g) - C_{p,m}^{\ominus}(C_2H_2, g) - C_{p,m}^{\ominus}(H_2, g)$$
$$= (43.56 - 43.93 - 28.82) \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$
$$= -29.19 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

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

E2.28(b)   NaCl, $AgNO_3$, and $NaNO_3$ are strong electrolytes, therefore the net ionic equation is

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

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

P2.24 $C_V = \left(\dfrac{\partial U}{\partial T}\right)_V$

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

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

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

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

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

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

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

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

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

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

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

P3.12

$$\Delta_r H^\ominus = \sum_{products} v\Delta_f H^\ominus - \sum_{reactants} v\Delta_f H^\ominus \quad [2.34a]$$

$$\Delta_r H^\ominus(298\ K) = 1 \times \Delta_f H^\ominus(CO,g) + 1 \times \Delta_f H^\ominus(H_2O,g) - 1 \times \Delta_f H^\ominus(CO_2,g)$$

$$= \{-110.53 - 241.82 - (-393.51)\}\ kJ\ mol^{-1} = \boxed{+41.16\ kJ\ mol^{-1}}$$

$$\Delta_r S^\ominus = \sum_{products} v S_m^\ominus - \sum_{reactants} v S_m^\ominus \quad [3.25a]$$

$$\Delta_r S^\ominus(298\ K) = 1 \times S_m^\ominus(CO,g) + 1 \times S_m^\ominus(H_2O,g) - 1 \times S_m^\ominus(CO_2,g) - 1 \times S_m^\ominus(H_2,g)$$

$$= (197.67 + 188.83 - 213.74 - 130.684)\ kJ\ mol^{-1} = \boxed{+42.08\ J\ K^{-1}\ mol^{-1}}$$

$$\Delta_r H^\ominus(398\ K) = \Delta_r H^\ominus(298\ K) + \int_{298\ K}^{398\ K} \Delta_r C_p^\ominus dT \quad [2.36a]$$

$$= \Delta_r H^\ominus(298\ K) + \Delta_r C_p^\ominus \Delta T \quad \text{[heat capacities constant]}$$

$$\Delta_r C_p^\ominus = 1 \times C_{p,m}^\ominus(CO,g) + 1 \times C_{p,m}^\ominus(H_2O,g) - 1 \times C_{p,m}^\ominus(CO_2,g) - 1 \times C_{p,m}^\ominus(H_2,g)$$
$$= (29.14 + 33.58 - 37.11 - 28.824)\ J\ K^{-1}\ mol^{-1} = -3.21\ J\ K^{-1}\ mol^{-1}$$

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

For each substance in the reaction

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

Thus,

$$\Delta_r S^\ominus(398\ K) = \Delta_r S^\ominus(298\ K) + \sum_{products} v C_{p,m}^\ominus \ln\left(\frac{T_f}{T_i}\right) - \sum_{reactants} v C_{p,m}^\ominus(J)\ln\left(\frac{T_f}{T_i}\right)$$

$$= \Delta_r S^\ominus(298\ K) + \Delta_r C_p^\ominus \ln\left(\frac{398\ K}{298\ K}\right)$$

$$= (42.08\ J\ K^{-1}\ mol^{-1}) + (-3.21\ J\ K^{-1}\ mol^{-1})\ln\left(\frac{398\ K}{298\ K}\right)$$

$$= (42.08 - 0.93)\ J\ K^{-1}\ mol^{-1} = \boxed{+41.15\ J\ K^{-1}\ mol^{-1}}$$

COMMENT. Both $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ 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
$(C_{p,m}/T)(J\ K^{-2}\ mol^{-1})$	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
$(C_{p,m}/T)(J\ K^{-2}\ mol^{-1})$	0.942	0.861	0.787	0.727	0.685	0.659

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

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

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

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

Solutions to problems

Solutions to numerical problems

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

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

At $T_1 = (273.15 - 29.2) \text{ K} = 244.0 \text{ K}$ (normal boiling point), $p_1 = 1.000$ 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) $\left(\dfrac{\partial \mu(l)}{\partial T}\right)_p - \left(\dfrac{\partial \mu(s)}{\partial T}\right)_p = -S_m(l) + S_m(s) = -\Delta_{fus}S = \dfrac{-\Delta_{fus}H}{T_f}$ [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) $\left(\dfrac{\partial \mu(g)}{\partial T}\right)_p - \left(\dfrac{\partial \mu(l)}{\partial T}\right)_p = -S_m(g) + S_m(l) = -\Delta_{vap}S = \dfrac{-\Delta_{vap}H}{T_b}$

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

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

because $\mu(l,0°C) = \mu(s,0°C)$

Thus, $\mu(l,-5°C) - \mu(s,-5°C) = \Delta\mu(l) - \Delta\mu(s)$

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

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

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

For DI

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

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

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

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

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

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

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

Then, from the first equation

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

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

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

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

which is close to the experimental value.

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

Therefore, since

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

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

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

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

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

so $\beta\varepsilon(J) = \theta_R J(J+1)/T$

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.

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

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:

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

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

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

Solutions to applications: astrophysics and biochemistry

P20.30   Newton's gravitational force law: $F = \dfrac{Gmm'}{r^2}$, 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 $g_{\text{planet}} = \dfrac{Gm'}{R^2}$ is the gravitational acceleration of a planet and $\dfrac{g_{\text{planet}}}{g_{\text{Earth}}} = \left(\dfrac{m}{R^2}\right)_{\text{planet}} \Big/ \left(\dfrac{m}{R^2}\right)_{\text{Earth}}$.

Using data provided in the problem:

$$g_{\text{Mars}} = g_{\text{Earth}} \times \left(\frac{m}{R^2}\right)_{\text{Mars}} \Big/ \left(\frac{m}{R^2}\right)_{\text{Earth}} = g_{\text{Earth}} \times \left(\frac{m_{\text{Mars}}}{m_{\text{Earth}}}\right) \times \left(\frac{R_{\text{Earth}}}{R_{\text{Mars}}}\right)^2$$

$$= (9.81 \text{ m s}^{-2}) \times (0.108) \times \left(\frac{6.37}{3.38}\right)^2 = 3.76 \text{ m s}^{-2}$$

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

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

(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: