20 Statistical thermodynamics: the machinery

Solutions to exercises

Discussion questions

E20.1(b) The symmetry number, σ, is a correction factor to prevent the over-counting of rotational states when computing the high temperature form of the rotational partition function. An elementary interpretation of σ is that it recognizes that in a homonuclear diatomic molecule AA the orientations AA$'$ and A$'$A are indistinguishable, and should not be counted twice, so the quantity $q = kT/hcB$ is replaced by $q = kT/\sigma hcB$ with $\sigma = 2$. A more sophisticated interpretation is that the Pauli principle allows only certain rotational states to be occupied, and the symmetry factor adjusts the high temperature form of the partition function (which is derived by taking a sum over all states), to account for this restriction. In either case the symmetry number is equal to the number of indistinguishable orientations of the molecule. More formally, it is equal to the order of the rotational subgroup of the molecule.

E20.2(b) The temperature is always high enough (provided the gas is above its condensation temperature) for the mean translational energy to be $\frac{3}{2}kT$. The equipartition value. Therefore, the molar constant-volume heat capacity for translation is $C_{V,m}^{T} = \frac{3}{2}R$.

Translation is the only mode of motion for a monatomic gas, so for such a gas $C_{V,m} = \frac{3}{2}R = 12.47\,\text{J K}^{-1}\,\text{mol}^{-1}$: This result is very reliable: helium, for example has this value over a range of 2000 K.

When the temperature is high enough for the rotations of the molecules to be highly excited (when $T \gg \theta_R$) we can use the equipartition value kT for the mean rotational energy (for a linear rotor) to obtain $C_{V,m} = R$. For nonlinear molecules, the mean rotational energy rises to $\frac{3}{2}kT$, so the molar rotational heat capacity rises to $\frac{3}{2}R$ when $T \gg \theta_R$. Only the lowest rotational state is occupied when the temperature is very low, and then rotation does not contribute to the heat capacity. We can calculate the rotational heat capacity at intermediate temperatures by differentiating the equation for the mean rotational energy (eqn 20.29). The resulting expression, which is plotted in Fig. 20.9 of the text shows that the contribution rises from zero (when $T = 0$) to the equipartition value (when $T \gg \theta_R$). Because the translational contribution is always present, we can expect the molar heat capacity of a gas of diatomic molecules ($C_{V,m}^{T} + C_{V,m}^{R}$) to rise from $\frac{3}{2}R$ to $\frac{5}{2}R$ as the temperature is increased above θ_R.

Molecular vibrations contribute to the heat capacity, but only when the temperature is high enough for them to be significantly excited. The equipartition mean energy is kT for each mode, so the maximum contribution to the molar heat capacity is R. However, it is very unusual for the vibrations to be so highly excited that equipartition is valid and it is more appropriate to use the full expression for the vibrational heat capacity which is obtained by differentiating eqn 20.32. The curve in Fig. 20.10 of the text shows how the vibrational heat capacity depends on temperature. Note that even when the temperature is only slightly above the vibrational temperature, the heat capacity is close to its equipartition value.

The total heat capacity of a molecular substance is the sum of each contribution (Fig. 20.11 of the text). When equipartition is valid (when the temperature is well above the characteristic temperature of the mode $T \gg \theta_M$) we can estimate the heat capacity by counting the numbers of modes that are active. In gases, all three translational modes are always active and contribute $3/2\,R$ to the molar heat capacity. If we denote the number of active rotational modes by ν_R^{*} (so for most molecules at normal temperatures $\nu_R^{*} = 2$ for linear molecules, and 3 for nonlinear molecules), then the rotational contribution is $1/2\,\nu_R^{*}R$. If the temperature is high enough for ν_V^{*} vibrational modes to be active the

vibrational contribution to the molar heat capacity is $\nu_R^* R$. In most cases $\nu_V \approx 0$. It follows that the total molar heat capacity is

$$C_{V,m} = \tfrac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R$$

E20.3(b) See *Justification* 20.4 for a derivation of the general expression (eqn 20.54) for the equilibrium constant in terms of the partition functions and difference in molar energy, $\Delta_r E_0$, of the products and reactants in a chemical reaction. The partition functions are functions of temperature and the ratio of partition functions in eqn 20.54 will therefore vary with temperature. However, the most direct effect of temperature on the equilibrium constant is through the exponential term $e^{-\Delta_r E_0/RT}$. The manner in which both factors affect the magnitudes of the equilibrium constant and its variation with temperature is described in detail for a simple R $\rightleftharpoons$ P gas phase equilibrium in Section 20.7(c) and *Justification* 20.5.

Numerical exercises

E20.4(b) $\quad C_{V,m} = \tfrac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R$ [20.40]

with a mode active if $T > \theta_M$. At low temperatures, the vibrational modes are not active, that is, $\nu_V^* = 0$; at high temperatures they are active and approach the equipartition value. Therefore

(a) $\quad O_3$: $\quad C_{V,m} = 3R \quad$ or $\quad 6R \quad (3 \times 3 - 6)$ vibrational modes

(b) $\quad C_2H_6$: $\quad C_{V,m} = 3R \quad$ or $\quad 21R \quad (3 \times 8 - 6)$ vibrational modes

(c) $\quad CO_2$: $\quad C_{V,m} = \tfrac{5}{2}R \quad$ or $\quad 6.5R \quad (3 \times 3 - 5)$ vibrational modes

where the first value applies to low temperatures and the second to high.

E20.5(b) The equipartition theorem would predict a contribution to molar heat capacity of $\tfrac{1}{2}R$ for every translational and rotational degree of freedom and R for each vibrational mode. For an ideal gas, $C_{p,m} = R + C_{V,m}$. So for CO_2

With vibrations $\quad C_{V,m}/R = 3\left(\tfrac{1}{2}\right) + 2\left(\tfrac{1}{2}\right) + (3 \times 4 - 6) = 6.5 \quad$ and $\quad \gamma = \dfrac{7.5}{6.5} = \boxed{1.15}$

Without vibrations $\quad C_{V,m}/R = 3\left(\tfrac{1}{2}\right) + 2\left(\tfrac{1}{2}\right) = 2.5 \quad$ and $\quad \gamma = \dfrac{3.5}{2.5} = \boxed{1.40}$

Experimental $\quad \gamma = \dfrac{37.11\,\text{J mol}^{-1}\,\text{K}^{-1}}{37.11 - 8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}} = \boxed{1.29}$

The experimental result is closer to that obtained by neglecting vibrations, but not so close that vibrations can be neglected entirely.

E20.6(b) The rotational partition function of a linear molecule is

$$q^R = \frac{kT}{\sigma hcB} = \frac{(1.381 \times 10^{-23}\,\text{J K}^{-1})T}{\sigma(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1})B} = \frac{0.6952(T/\text{K})}{\sigma B/\text{cm}^{-1}}$$

(a) At 25°C $\quad q^R = \dfrac{0.6952(25 + 273)}{1.4457} = \boxed{143}$

(b) At 250°C $\quad q^R = \dfrac{0.6952(250 + 273)}{1.4457} = \boxed{251}$

E20.7(b) The symmetry number is the order of the rotational subgroup of the group to which a molecule belongs (except for linear molecules, for which $\sigma = 2$ if the molecule has inversion symmetry and 1 otherwise).

(a) CO_2: Full group $D_{\infty h}$; subgroup C_2 $\boxed{\sigma = 2}$ (d) SF_6: O_h $\boxed{\sigma = 24}$

(b) O_3: Full group C_{2v}; subgroup C_2 $\boxed{\sigma = 2}$ (e) Al_2Cl_6: D_{2d} $\boxed{\sigma = 4}$

(c) SO_3: Full group D_{3h}; subgroup $\{E, C_3, C_3^2, 3C_2\}$ $\boxed{\sigma = 6}$

E20.8(b)   The rotational partition function of nonlinear molecule is given by

$$
\begin{aligned}
q^R &= \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2} \\
&= \frac{1}{2}\left(\frac{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (298\,\text{K})}{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1})}\right)^{3/2} \\
&\quad \times \left(\frac{\pi}{(2.02736) \times (0.34417) \times (0.293535)\,\text{cm}^{-3}}\right)^{1/2} = \boxed{5.84 \times 10^3}
\end{aligned}
$$

This high-temperature approximation is valid if $T \gg \theta_R$, where θ_R, the rotational temperature, is

$$
\begin{aligned}
\theta_R &= \frac{hc(ABC)^{1/3}}{k} \\
&= \frac{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1})}{1.381 \times 10^{-23}\,\text{J K}^{-1}} \\
&\quad \times [(2.02736) \times (0.34417) \times (0.293535)\,\text{cm}^{-3}]^{1/3} \\
&= \boxed{0.8479\,\text{K}}
\end{aligned}
$$

E20.9(b) $q^R = 583\overline{7}$ [Exercise 20.8(b)]

All rotational modes of SO_2 are active at $25°C$; therefore

$$
U_m^R - U_m^R(0) = E^R = \tfrac{3}{2}RT
$$

$$
\begin{aligned}
S_m^R &= \frac{E^R}{T} + R \ln q^R \\
&= \tfrac{3}{2}R + R\ln(583\overline{6.9}) = \boxed{84.57\,\text{J K}^{-1}\,\text{mol}^{-1}}
\end{aligned}
$$

E20.10(b)   (a) The partition function is

$$
q = \sum_{\text{states}} e^{-E_{\text{state}}/kT} = \sum_{\text{levels}} g e^{-E_{\text{level}}/kT}
$$

where g is the degeneracy of the level. For rotations of a symmetric rotor such as CH_3CN, the energy levels are $E_J = hc[BJ(J+1)+(A-B)K^2]$ and the degeneracies are $g_{J,K} = 2(2J+1)$ if $K \neq 0$ and $2J+1$ if $K = 0$. The partition function, then, is

$$
q = 1 + \sum_{J=1}^{\infty}(2J+1)e^{-\{hcBJ(J+1)/kT\}}\left(1 + 2\sum_{K=1}^{J} e^{-\{hc(A-B)K^2/kT\}}\right)
$$

To evaluate this sum explicitly, we set up the following columns in a spreadsheet (values for $B = 5.2412\,\text{cm}^{-1}$ and $T = 298.15\,\text{K}$)

J	$J(J+1)$	$2J+1$	$e^{-\{hcBJ(J+1)/kT\}}$	J term	$e^{-\{hc(A-B)K^2/kT\}}$	K sum	J sum
0	0	1	1	1	1	1	1
1	2	3	0.997	8.832	0.976	2.953	9.832
2	6	5	0.991	23.64	0.908	4.770	33.47
3	12	7	0.982	43.88	0.808	6.381	77.35
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
82	6806	165	4.18×10^{-5}	0.079	8×10^{-71}	11.442	7498.95
83	6972	167	3.27×10^{-5}	0.062	2×10^{-72}	11.442	7499.01

The column labelled K sum is the term in large parentheses, which includes the inner summation. The J sum converges (to 4 significant figures) only at about $J = 80$; the K sum converges much more quickly. But the sum fails to take into account nuclear statistics, so it must be divided by the symmetry number. At 298 K, $q^R = \boxed{2.50 \times 10^3}$. A similar computation at $T = 500$ K yields $q^R = \boxed{5.43 \times 10^3}$.

(b) The rotational partition function of a nonlinear molecule is given by

$$q^R = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2}$$

At 298 K $q^R = \frac{1}{3}\left(\frac{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (298\,\text{K})}{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1})}\right)^{3/2}$

$$\times \left(\frac{\pi}{(5.28) \times (0.307)^2\,\text{cm}^{-3}}\right)^{1/2}$$

$$= \boxed{2.50 \times 10^3}$$

At 500 K $q^R = \frac{1}{3}\left(\frac{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (500\,\text{K})}{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1})}\right)^{3/2}$

$$\times \left(\frac{\pi}{(5.28) \times (0.307)^2\,\text{cm}^{-3}}\right)^{1/2}$$

$$= \boxed{5.43 \times 10^3}$$

E20.11(b) The rotational partition function of a nonlinear molecule is given by

$$q^R = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2}$$

(a) At 25°C

$$q^R = \frac{1}{1}\left(\frac{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (298\,\text{K})}{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1})}\right)^{3/2}$$

$$\times \left(\frac{\pi}{(3.1252) \times (0.3951) \times (0.3505)\,\text{cm}^{-3}}\right)^{1/2}$$

$$= \boxed{8.03 \times 10^3}$$

(b) At $100°C$

$$q^R = \frac{1}{1} \left(\frac{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (373\,\text{K})}{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1})} \right)^{3/2}$$

$$\times \left(\frac{\pi}{(3.1252) \times (0.3951) \times (0.3505)\,\text{cm}^{-3}} \right)^{1/2}$$

$$= \boxed{1.13 \times 10^4}$$

E20.12(b) The molar entropy of a collection of oscillators is given by

$$S_m = \frac{N_A \langle \varepsilon \rangle}{T} + R \ln q$$

where $\langle \varepsilon \rangle = \dfrac{hc\tilde{\nu}}{e^{\beta hc\tilde{\nu}} - 1} = k\dfrac{\theta}{e^{\theta/T} - 1}$ and $q = \dfrac{1}{1 - e^{-\beta hc\tilde{\nu}}} = \dfrac{1}{1 - e^{-\theta/T}}$

where θ is the vibrational temperature $hc\tilde{\nu}/k$. Thus

$$S_m = \frac{R(\theta/T)}{e^{\theta/T}} - R \ln(1 - e^{-\theta/T})$$

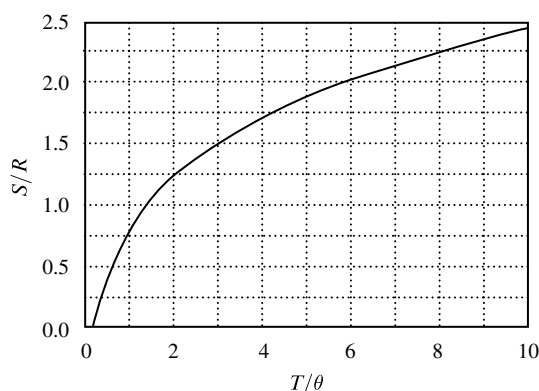A plot of S_m/R versus T/θ is shown in Fig. 20.1.

Figure 20.1

The vibrational entropy of ethyne is the sum of contributions of this form from each of its seven normal modes. The table below shows results from a spreadsheet programmed to compute S_m/R at a given temperature for the normal-mode wavenumbers of ethyne.

		$T = 298\,\text{K}$		$T = 500\,\text{K}$	
$\tilde{\nu}/\text{cm}^{-1}$	θ/K	T/θ	S_m/R	T/θ	S_m/R
612	880	0.336	0.208	0.568	0.491
729	1049	0.284	0.134	0.479	0.389
1974	2839	0.105	0.000766	0.176	0.0228
3287	4728	0.0630	0.00000217	0.106	0.000818
3374	4853	0.0614	0.00000146	0.103	0.000652

The total vibrational heat capacity is obtained by summing the last column (twice for the first two entries, since they represent doubly degenerate modes).

(a) At 298 K $\quad S_m = 0.685R = \boxed{5.70\,\text{J mol}^{-1}\,\text{K}^{-1}}$

(b) At 500 K $\quad S_m = 1.784R = \boxed{14.83\,\text{J mol}^{-1}\,\text{K}^{-1}}$

E20.13(b) The contributions of rotational and vibrational modes of motion to the molar Gibbs energy depend on the molecular partition functions

$$G_m - G_m(0) = -RT \ln q$$

The rotational partition function of a nonlinear molecule is given by

$$q^R = \frac{1}{\sigma} \left(\frac{kT}{hc}\right)^{3/2} \left(\frac{\pi}{ABC}\right)^{1/2} = \frac{1.0270}{\sigma} \left(\frac{(T/\text{K})^3}{ABC/\text{cm}^{-3}}\right)^{1/2}$$

and the vibrational partition function for each vibrational mode is given by

$$q^V = \frac{1}{1 - e^{-\theta/T}} \quad \text{where } \theta = hc\tilde{\nu}/k = 1.4388(\tilde{\nu}/\text{cm}^{-1})/(T/\text{K})$$

At 298 K $\quad q^R = \frac{1.0270}{2} \left(\frac{298^3}{(3.553) \times (0.4452) \times (0.3948)}\right)^{1/2} = 3.35 \times 10^3$

and $\quad G_m^R - G_m^R(0) = -(8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}) \times (298\,\text{K}) \ln 3.35 \times 10^3$

$$= -20.1 \times 10^3\,\text{J mol}^{-1} = \boxed{-20.1\,\text{kJ mol}^{-1}}$$

The vibrational partition functions are so small that we are better off taking

$$\ln q^V = -\ln(1 - e^{-\theta/T}) \approx e^{-\theta/T}$$
$$\ln q_1^V \approx e^{-\{1.4388(1110)/298\}} = 4.70 \times 10^{-3}$$
$$\ln q_2^V \approx e^{-\{1.4388(705)/298\}} = 3.32 \times 10^{-2}$$
$$\ln q_3^V \approx e^{-\{1.4388(1042)/298\}} = 6.53 \times 10^{-3}$$

so $G_m^V - G_m^V(0) = -(8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}) \times (298\,\text{K}) \times (4.70 \times 10^{-3} + 3.32 \times 10^{-2} + 6.53 \times 10^{-3})$

$$= -110\,\text{J mol}^{-1} = \boxed{-0.110\,\text{kJ mol}^{-1}}$$

E20.14(b) $q = \sum_j g_j e^{-\beta \varepsilon_j}, \quad g = (2S+1) \times \begin{cases} 1 \text{ for } \Sigma \text{ states} \\ 2 \text{ for } \Pi, \Delta, \dots \text{ states} \end{cases}$ [Section 17.1]

Hence

$q = 3 + 2e^{-\beta \varepsilon}$ [the $^3\Sigma$ term is triply degenerate, and the $^1\Delta$ term is doubly (orbitally) degenerate]

At 400 K

$$\beta \varepsilon = \frac{(1.4388\,\text{cm K}) \times (7918.1\,\text{cm}^{-1})}{400\,\text{K}} = 28.48$$

Therefore, the contribution to G_m is

$G_m - G_m(0) = -RT \ln q$ [Table 20.1, $n = 1$]

$-RT \ln q = (-8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (400\,\text{K}) \times \ln(3 + 2 \times e^{-28.48})$

$$= (-8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (400\,\text{K}) \times (\ln 3) = \boxed{-3.65\,\text{kJ mol}^{-1}}$$

E20.15(b) The degeneracy of a species with $S = \frac{5}{2}$ is 6. The electronic contribution to molar entropy is

$$S_m = \frac{U_m - U_m(0)}{T} + R \ln q = R \ln q$$

(The term involving the internal energy is proportional to a temperature-derivative of the partition function, which in turn depends on excited state contributions to the partition function; those contributions are negligible.)

$$S_m = (8.3145\, \text{J mol}^{-1}\, \text{K}^{-1}) \ln 6 = \boxed{14.9\, \text{J mol}^{-1}\, \text{K}^{-1}}$$

E20.16(b) Use $S_m = R \ln s$ [20.52]
Draw up the following table

n:	0	1	2			3			4			5	6
			o	m	p	a	b	c	o	m	p		
s	1	6	6	6	3	6	6	2	6	6	3	6	1
S_m/R	0	1.8	1.8	1.8	1.1	1.8	1.8	0.7	1.8	1.8	1.1	1.8	0

where a is the 1, 2, 3 isomer, b the 1, 2, 4 isomer, and c the 1, 3, 5 isomer.

E20.17(b) We need to calculate

$$K = \prod_J \left(\frac{q_{J,m}^{\ominus}}{N_A} \right)^{\nu_J} \times e^{-\Delta E_0/RT} \quad [\textit{Justification } 20.4]$$

$$= \frac{q_m^{\ominus}(^{79}\text{Br}_2) q_m^{\ominus}(^{81}\text{Br}_2)}{q_m^{\ominus}(^{79}\text{Br}^{81}\text{Br})^2} e^{-\Delta E_0/RT}$$

Each of these partition functions is a product

$$q_m^T q^R q^V q^E$$

with all $q^E = 1$.

The ratio of the translational partition functions is virtually 1 (because the masses nearly cancel; explicit calculation gives 0.999). The same is true of the vibrational partition functions. Although the moments of inertia cancel in the rotational partition functions, the two homonuclear species each have $\sigma = 2$, so

$$\frac{q^R(^{79}\text{Br}_2) q^R(^{81}\text{Br}_2)}{q^R(^{79}\text{Br}^{81}\text{Br})^2} = 0.25$$

The value of ΔE_0 is also very small compared with RT, so

$$K \approx \boxed{0.25}$$

Solutions to problems

Solutions to numerical problems

P20.2 $\Delta\varepsilon = \varepsilon = g\mu_B \mathcal{B}$ [18.48, Section 18.14]

$q = 1 + e^{-\beta\varepsilon}$

$C_{V,m}/R = \dfrac{x^2 e^{-x}}{(1 + e^{-x})^2}$ [Problem 20.1], $\quad x = 2\mu_B \mathcal{B}\beta \quad [g = 2]$

Therefore, if $\mathcal{B} = 5.0\,\text{T}$,

$$x = \frac{(2) \times (9.274 \times 10^{-24}\,\text{J T}^{-1}) \times (5.0\,\text{T})}{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times T} = \frac{6.72}{T/\text{K}}$$

(a) $T = 50\,\text{K}$, $x = 0.134$, $C_V = 4.47 \times 10^{-3}R$, implying that $C_V = 3.7 \times 10^{-2}\,\text{J K}^{-1}\,\text{mol}^{-1}$. Since the equipartition value is about $3R$ [$\nu_R^* = 3$, $\nu_V^* \approx 0$], the field brings about a change of about $\boxed{0.1 \text{ per cent}}$

(b) $T = 298\,\text{K}$, $x = 2.26 \times 10^{-2}$, $C_V = 1.3 \times 10^{-4}R$, implying that $C_V = 1.1\,\text{mJ K}^{-1}\,\text{mol}^{-1}$, a change of about $\boxed{4 \times 10^{-3} \text{ per cent}}$

Question. What percentage change would a magnetic field of 1 kT cause?

P20.4 $q = 1 + 5\text{e}^{-\beta\varepsilon}$ $[g_j = 2J + 1]$

$\varepsilon = E(J = 2) - E(J = 0) = 6hcB$ $[E = hcBJ(J + 1)]$

$\dfrac{U - U(0)}{N} = -\dfrac{1}{q}\dfrac{\partial q}{\partial \beta} = \dfrac{5\varepsilon\text{e}^{-\beta\varepsilon}}{1 + 5\text{e}^{-\beta\varepsilon}}$

$C_{V,\text{m}} = -k\beta^2 \left(\dfrac{\partial U_\text{m}}{\partial \beta}\right)_V$ [20.35]

$C_{V,\text{m}}/R = \dfrac{5\varepsilon^2\beta^2\text{e}^{-\beta\varepsilon}}{(1 + 5\text{e}^{-\beta\varepsilon})^2} = \dfrac{180(hcB\beta)^2\text{e}^{-6hcB\beta}}{(1 + 5\text{e}^{-6hcB\beta})^2}$

$\dfrac{hcB}{k} = 1.4388\,\text{cm K} \times 60.864\,\text{cm}^{-1} = 87.571\,\text{K}$

Hence,

$$C_{V,\text{m}}/R = \frac{1.380 \times 10^6 \text{e}^{-525.4\,\text{K}/T}}{(1 + 5\text{e}^{-525.4\,\text{K}/T}) \times (T/\text{K})^2}$$

We draw up the following table

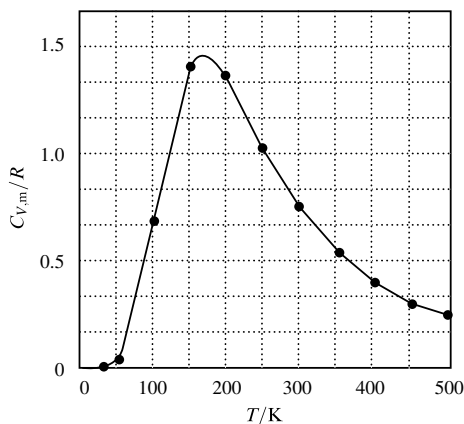| T/K	50	100	150	200	250	300	350	400	450	500
$C_{V,\text{m}}/R$	0.02	0.68	1.40	1.35	1.04	0.76	0.56	0.42	0.32	0.26

These points are plotted in Fig. 20.2.

Figure 20.2

P20.6
$$\frac{q_m^T}{N_A} = 2.561 \times 10^{-2} \times (T/K)^{5/2} \times (M/\text{g mol}^{-1})^{3/2} \quad [\text{Table 20.3}]$$

$$= (2.561 \times 10^{-2}) \times (298)^{5/2} \times (28.02)^{3/2} = 5.823 \times 10^6$$

$$q^R = \frac{1}{2} \times 0.6950 \times \frac{298}{1.9987}[\text{Table 20.3}] = 51.81$$

$$q^V = \frac{1}{1 - e^{-2358/207.2}}[\text{Table 20.3}] = 1.00$$

Therefore

$$\frac{q_m^{\ominus}}{N_A} = (5.82\overline{3} \times 10^6) \times (51.8\overline{1}) \times (1.00) = 3.02 \times 10^8$$

$$U_m - U_m(0) = \tfrac{3}{2}RT + RT = \tfrac{5}{2}RT \quad [T \gg \theta_T, \theta_R]$$

Hence

$$S_m^{\ominus} = \frac{U_m - U_m(0)}{T} + R\left(\ln \frac{q_m^{\ominus}}{N_A} + 1\right)$$

$$= \tfrac{5}{2}R + R\{\ln 3.02 \times 10^8 + 1\} = 23.03R = \boxed{191.4\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

The difference between the experimental and calculated values is negligible, indicating that the residual entropy is negligible.

P20.9   **(a)** Rotational state probability distribution,

$$P_J^R(T) = \frac{(2J+1)e^{-hcBJ(J+1)/kT}}{\displaystyle\sum_{J=0}(2J+1)e^{-hcBJ(J+1)/kT}}, \quad [20.14]$$

is conveniently plotted against J at several temperatures using mathematical software. This distribution at 100 K is shown below as both a bar plot and a line plot.
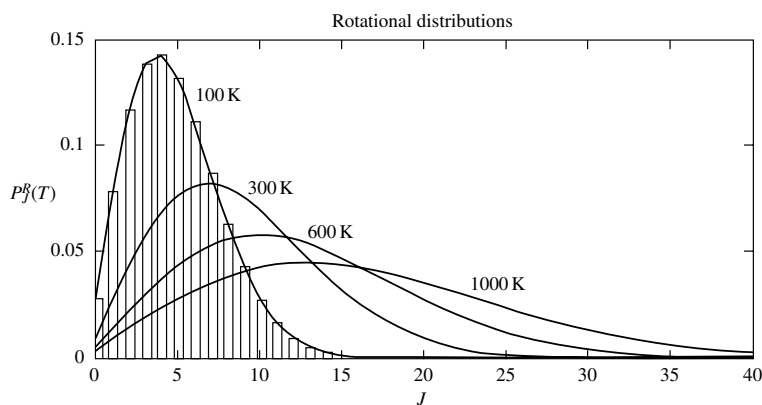

Figure 20.3(a)

The plots show that higher rotational states become more heavily populated at higher temperature. Even at 100 K the most populated state has 4 quanta of rotational energy; it is elevated to 13 quanta at 1000 K.

Values of the vibrational state probability distribution,

$$P_v^V(T) = e^{-vhc\tilde{v}/kT}(1 - e^{-hc\tilde{v}/kT})^{-1}, \quad [20.21]$$

are conveniently tabulated against v at several temperatures. Computations may be discontinued when values drop below some small number like 10^{-7}.

	$P_v^V(T)$			
v	100 K	300 K	600 K	1000 K
0	1	1	0.995	0.956
1	2.77×10^{-14}	3.02×10^{-5}	5.47×10^{-3}	0.042
2		9.15×10^{-10}	3.01×10^{-5}	1.86×10^{-3}
3			1.65×10^{-7}	8.19×10^{-5}
4				3.61×10^{-6}
5				1.59×10^{-7}

Only the state $v = 0$ is appreciably populated below 1000 K and even at 1000 K only 4% of the molecules have 1 quanta of vibrational energy.

(b) $$\theta_R = \frac{hcB}{k} = \frac{(6.626 \times 10^{-34}\,\text{J s})(3.000 \times 10^8\,\text{m s}^{-1})(193.1\,\text{m}^{-1})}{1.381 \times 10^{-23}\,\text{J K}^{-1}} \quad \text{(Section 20.2b)}$$

$$\theta_R = 2.779\,\text{K}$$

Since $\theta_R \ll T$ where T is the lowest temperature of current interest (100 K), we expect that the classical rotational partition function,

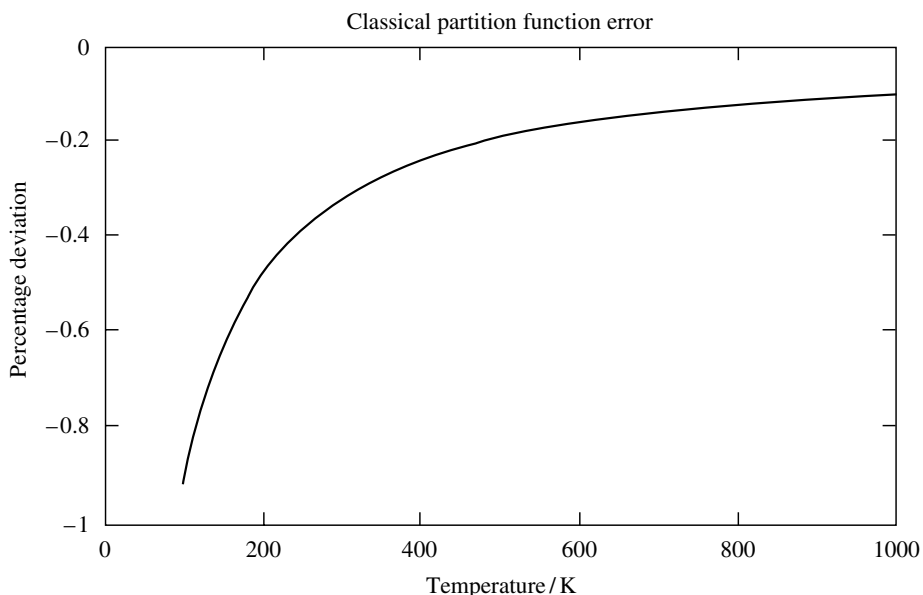$$q_{classical}^R(T) = \frac{kT}{hcB}, \quad [20.15a]$$

Figure 20.3(a)

should agree well with the rotational partition function calculated with the discrete energy distribution,

$$q^R = \sum_{J=0} (2J + 1)e^{-hcBJ(J+1)/kT}. \quad [20.14]$$

A plot of the percentage deviation $(q^R_{classical} - q^R)100/q^R$ confirms that they agree. The maximum deviation is about -0.9% at 100 K and the magnitude decreases with increasing temperature.

(c) The translational, rotational, and vibrational contributions to the total energy are specified by eqns 20.28, 20.30, and 20.32. As molar quantities, they are:

$$U^T = \tfrac{3}{2}RT, \quad U^R = RT, \quad U^V = \frac{N_A hc\tilde{\nu}}{e^{hc\tilde{\nu}/kT} - 1}$$

The contributions to the energy change from 100 K are $\Delta U^T(T) = U^T(T) - U^T(100\,\text{K})$, etc. The following graph shows the individual contributions to the total molar internal energy change from 100 K. Translational motion contributes 50% more than the rotational motion because it has 3 quadratic degrees of freedom compared to 2 quadratic degrees of freedom for rotation. Very little change occurs in the vibration energy because very high temperatures are required to populate $\nu = 1, 2, \ldots$ states (see Part a).

$$C_{V,m}(T) = \left(\frac{\partial U(T)}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\right)_V (U^T + U^R + U^V) \quad [2.19]$$

$$= \frac{3}{2}R + R + \frac{dU^V}{dT} = \frac{5}{2}R + \frac{dU^V}{dT}$$
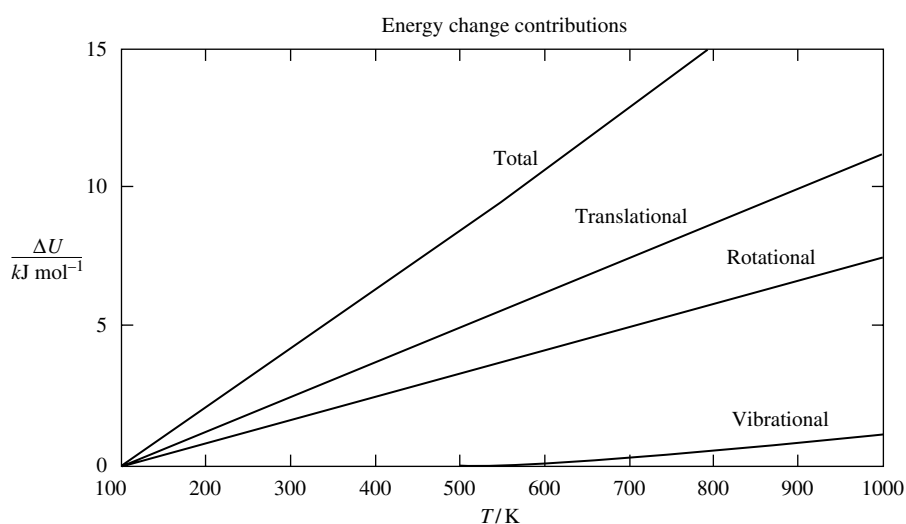

Figure 20.3(c)

The derivative dU^V/dT may be evaluated numerically with numerical software (we advise exploration of the technique) or it may be calculated with the analytical function of eqn 20.39:

$$C_{V,m}^V = \frac{dU^V}{dT} = R \left\{ \frac{\theta_V}{T} \left(\frac{e^{-\theta_V/2T}}{1 - e^{-\theta_V/T}} \right) \right\}^2$$

where $\theta_V = hc\tilde{\nu}/k = 3122\,\text{K}$. The following graph shows the ratio of the vibrational contribution to the sum of translational and rotational contributions. Below 300 K, vibrational motions makes a small, perhaps negligible, contribution to the heat capacity. The contribution is about 10% at 600 K and grows with increasing temperature.

Relative contributions to the heat capacity
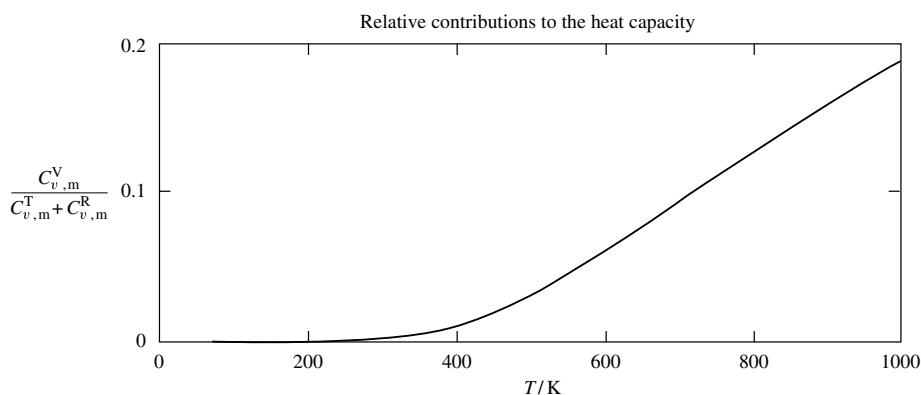
Figure 20.3(d)

The molar entropy change with temperature may be evaluated by numerical integration with mathematical software.

$$\Delta S(T) = S(T) - S(100\,\text{K}) = \int_{100\,\text{K}}^{T} \frac{C_{p,m}(T)\,dT}{T} \qquad [4.19]$$

$$= \int_{100\,\text{K}}^{T} \frac{C_{V,m}(T) + R}{T}\,dT \qquad [3.20]$$

$$= \int_{100\,\text{K}}^{T} \frac{\frac{7}{2}R + C_{V,m}^V(T)}{T}\,dT$$

$$\Delta S(T) = \underbrace{\frac{7}{2}R \ln\left(\frac{T}{100\,\text{K}}\right)}_{\Delta S^{T+R}(T)} + \underbrace{\int_{100\,\text{K}}^{T} \frac{C_{V,m}^V(T)}{T}\,dT}_{\Delta S^V(T)}$$

Even at the highest temperature the vibrational contribution to the entropy change is less than 2.5% of the contributions from translational and rotational motion.

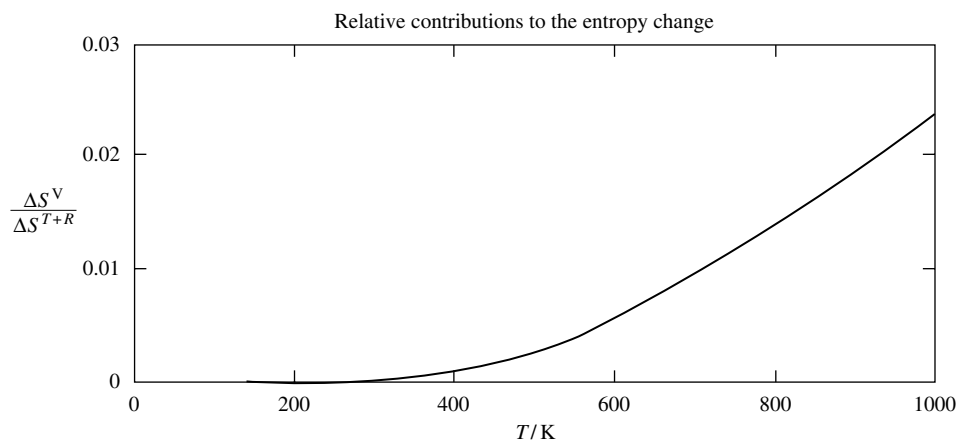The vibrational contribution is negligible at low temperature.

Relative contributions to the entropy change

Figure 20.3(e)

P20.10

$$K = \frac{q_m^{\ominus}(CHD_3)q_m^{\ominus}(DCl)}{q_m^{\ominus}(CD_4)q_m^{\ominus}(HCl)}e^{-\beta\Delta E_0} \text{ [20.54, } N_A \text{ factors cancel]}$$

The ratio of translational partition functions is

$$\frac{q_m^T(CHD_3)q_m^T(DCl)}{q_m^T(CD_4)q_m^T(HCl)} = \left(\frac{M(CHD_3)M(DCl)}{M(CD_4)M(HCl)}\right)^{3/2} = \left(\frac{19.06 \times 37.46}{20.07 \times 36.46}\right)^{3/2} = 0.964$$

The ratio of rotational partition functions is

$$\frac{q^R(CHD_3)q^R(DCl)}{q^R(CD_4)q^R(HCl)} = \frac{\sigma(CD_4)}{\sigma(CHD_3)}\frac{(B(CD_4)/cm^{-1})^{3/2}B(HCl)/cm^{-1}}{(A(CHD_3)B(CHD_3)^2/cm^{-3})^{1/2}B(DCl)/cm^{-1}}$$

$$= \frac{12}{3} \times \frac{2.63^{3/2} \times 10.59}{(2.63 \times 3.28^2)^{1/2} \times 5.445} = 6.24$$

The ratio of vibrational partition functions is

$$\frac{q^V(CHD_3)q^V(DCl)}{q^V(CD_4)q^V(HCl)} = \frac{q(2993)q(2142)q(1003)^3q(1291)^2q(1036)^2q(2145)}{q(2109)q(1092)^2q(2259)^3q(996)^3q(2991)}$$

where $q(x) = \dfrac{1}{1 - e^{-1.4388x/(T/K)}}$

We also require ΔE_0, which is equal to the difference in zero point energies

$$\frac{\Delta E_0}{hc} = \frac{1}{2}\{(2993 + 2142 + 3 \times 1003 + 2 \times 1291 + 2 \times 1036 + 2145)$$

$$- (2109 + 2 \times 1092 + 3 \times 2259 + 3 \times 996 + 2991)\}\,cm^{-1}$$

$$= -1053\,cm^{-1}$$

Hence,

$$K = 0.964 \times 6.24 \times Qe^{+1.4388 \times 990/(T/K)} = 6.02Qe^{+1424/(T/K)}$$

where Q is the ratio of vibrational partition functions. We can now evaluate K (on a computer), and obtain the following values

T/K	300	400	500	600	700	800	900	1000
K	698	217	110	72	54	44	38	34

The values of K are plotted in Fig. 20.4.
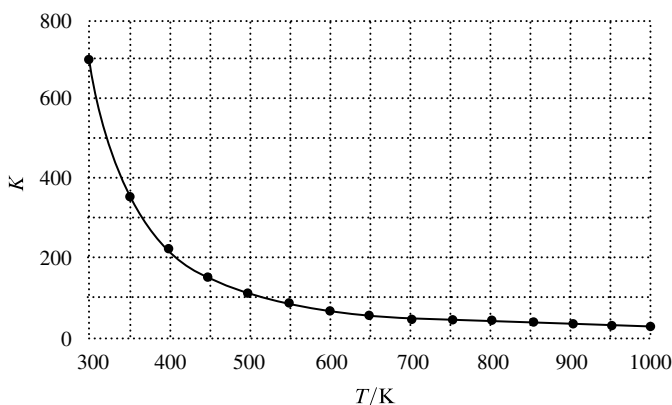
Figure 20.4

Solutions to theoretical problems

P20.13   (a) θ_V and θ_R are the constant factors in the numerators of the negative exponents in the sums that are the partition functions for vibration and rotation. They have the dimensions of temperature which occurs in the denominator of the exponents. So high temperature means $T \gg \theta_V$ or θ_R and only then does the exponential become substantial. Thus θ_V is a measure of the temperature at which higher vibrational and rotational states become populated.

$$\theta_R = \frac{hc\beta}{k} = \frac{(2.998 \times 10^8\,\text{m s}^{-1}) \times (6.626 \times 10^{-34}\,\text{J s}) \times (60.864\,\text{cm}^{-1})}{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (1\,\text{m}/100\,\text{cm})}$$
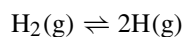
$$= \boxed{87.55\,\text{K}}$$

$$\theta_V = \frac{hc\tilde{v}}{k} = \frac{(6.626 \times 10^{-34}\,\text{J s}) \times (4400.39\,\text{cm}^{-1}) \times (2.998 \times 10^8\,\text{m s}^{-1})}{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (1\,\text{m}/100\,\text{cm})}$$

$$= \boxed{6330\,\text{K}}$$

(b) and (c)   These parts of the solution were performed with Mathcad 7.0 and are reproduced on the following pages.

Objective: To calculate the equilibrium constant $K(T)$ and $C_p(T)$ for dihydrogen at high temperature for a system made with n mol H_2 at 1 bar.

$$H_2(g) \rightleftharpoons 2H(g)$$

At equilibrium the degree of dissociation, α, and the equilibrium amounts of H_2 and atomic hydrogen are related by the expressions

$$n_{H_2} = (1 - \alpha)n \quad \text{and} \quad n_H = 2\alpha n$$

The equilibrium mole fractions are

$$x_{H_2} = (1 - \alpha)n/\{(1 - \alpha)n + 2\alpha n\} = (1 - \alpha)/(1 + \alpha)$$

$$x_H = 2\alpha n/\{(1 - \alpha)n + 2\alpha n\} = 2\alpha/(1 + \alpha)$$

The partial pressures are

$$p_{H_2} = (1 - \alpha)p/(1 + \alpha) \quad \text{and} \quad p_H = 2\alpha p/(1 + \alpha)$$

The equilibrium constant is

$$K(T) = (p_H/p^{\ominus})^2/(p_{H_2}/p^{\ominus}) = 4\alpha^2(p/p^{\ominus})/(1 - \alpha^2)$$

$$= 4\alpha^2/(1 - \alpha^2) \quad \text{where } p = p^{\ominus} = 1 \text{ bar}$$

The above equation is easily solved for α

$$\boxed{\alpha = (K/(K + 4))^{1/2}}$$

The heat capacity at constant volume for the equilibrium mixture is

$$C_V(\text{mixture}) = n_H C_{V,m}(H) + n_{H_2} C_{V,m}(H_2)$$

The heat capacity at constant volume per mole of dihydrogen used to prepare the equilibrium mixture is

$$C_V = C_V(\text{mixture})/n = \{n_H C_{V,m}(H) + n_{H_2} C_{V,m}(H_2)\}/n$$

$$= \boxed{2\alpha C_{V,m}(H) + (1 - \alpha)C_{V,m}(H_2)}$$

The formula for the heat capacity at constant pressure per mole of dihydrogen used to prepare the equilibrium mixture (C_p) can be deduced from the molar relationship

$$C_{p,m} = C_{V,m} + R$$

$$C_p = \{n_H C_{p,m}(H) + n_{H_2} C_{p,m}(H_2)\}/n$$

$$= \frac{n_H}{n}\{C_{V,m}(H) + R\} + \frac{n_{H_2}}{n}\{C_{V,m}(H_2) + R\}$$

$$= \frac{n_H C_{V,m}(H) + n_{H_2} C_{V,m}(H_2)}{n} + R\left(\frac{n_H + n_{H_2}}{n}\right)$$

$$= C_V + R(1 + \alpha)$$

Calculations

J = joule	s = second	kJ = 1000 J
mol = mole	g = gram	bar = 1×10^5 Pa
$h = 6.62608 \times 10^{-34}$ J s	$c = 2.9979 \times 10^8$ m s^{-1}	$k = 1.38066 \times 10^{-23}$ J K^{-1}
$R = 8.31451$ J K^{-1} mol^{-1}	$N_A = 6.02214 \times 10^{23}$ mol^{-1}	$p^{\ominus} = 1$ bar

Molecular properties of H_2

$$\nu = 4400.39 \text{ cm}^{-1} \quad B = 60.864 \text{ cm}^{-1} \quad D = 432.1 \text{ kJ mol}^{-1}$$

$$m_H = \frac{1 \text{ g mol}^{-1}}{N_A} \quad m_{H_2} = 2m_H$$

$$\theta_V = \frac{hc\nu}{k} \quad \theta_R = \frac{hcB}{k}$$

Computation of $K(T)$ and $\alpha(T)$

$$N = 200 \qquad i = 0, \ldots, N \qquad T_i = 500\,\text{K} + \frac{i \times 5500\,\text{K}}{N}$$

$$\Lambda_{\text{H}_i} = \frac{h}{(2\pi m_{\text{H}} k T_i)^{1/2}} \qquad \Lambda_{\text{H}_{2i}} = \frac{h}{(2\pi m_{\text{H}_2} k T_i)^{1/2}}$$

$$q_{V_i} = \frac{1}{1 - e^{-(\theta_{\text{V}}/T_i)}} \qquad q_{R_i} = \frac{T_i}{2\theta_{\text{R}}}$$

$$\boxed{K_{\text{eq}_i} = \frac{kT_i \left(\Lambda_{\text{H}_{2i}}\right)^3 e^{-(D/RT_i)}}{p^{\ominus} q_{V_i} q_{R_i} \left(\Lambda_{\text{H}_i}\right)^6}} \qquad \alpha_i = \left(\frac{K_{\text{eq}_i}}{K_{\text{eq}_i} + 4}\right)^{1/2}$$

See Fig. 20.5(a) and (b).
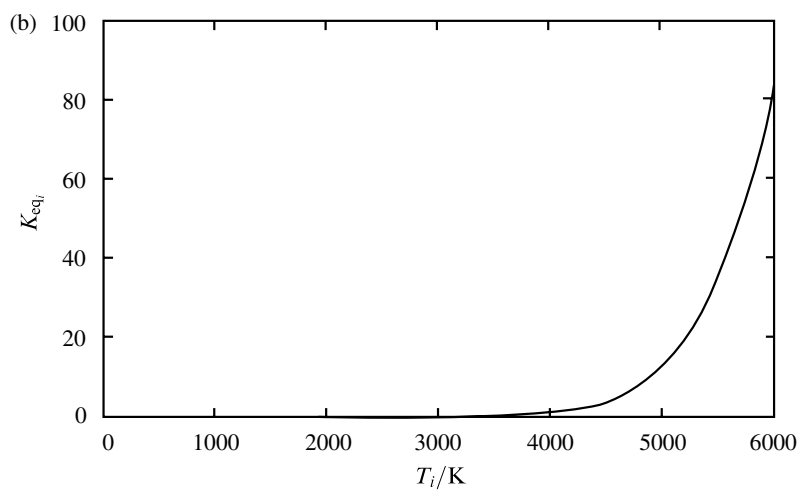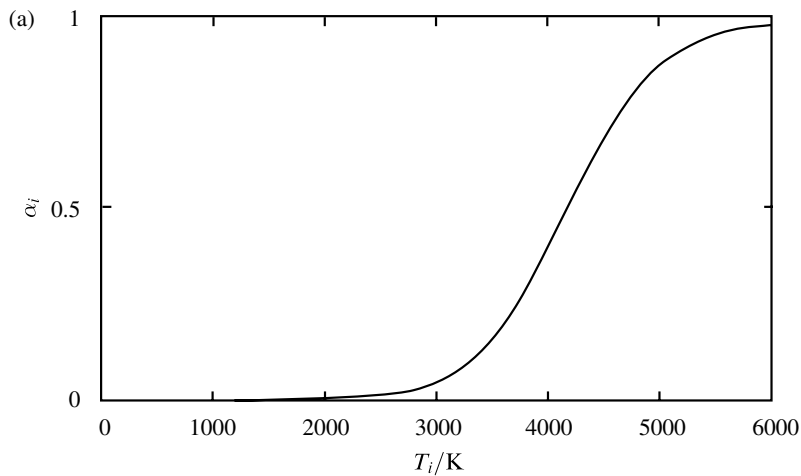

Figure 20.5

Heat capacity at constant volume per mole of dihydrogen used to prepare equilibrium mixture (see Fig. 20.6(a))
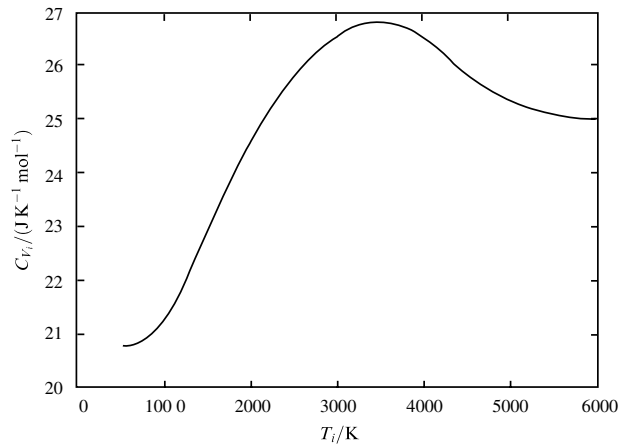

<div align="right">**Figure 20.6(a)**</div>

$$C_V(\text{H}) = \boxed{1.5R}$$

$$C_V(\text{H}_{2_i}) = \boxed{2.5R + \left[\frac{\theta_\text{V}}{T_i} \times \frac{e^{-(\theta_\text{V}/2T_i)}}{1 - e^{-(\theta_\text{V}/T_i)}} \right]^2 R} \qquad C_{V_i} = 2\alpha_i C_V(\text{H}) + (1 - \alpha_i)C_V(\text{H}_{2_i})$$

The heat capacity at constant pressure per mole of dihydrogen used to prepare the equilibrium mixture is (see Fig. 20.6(b))

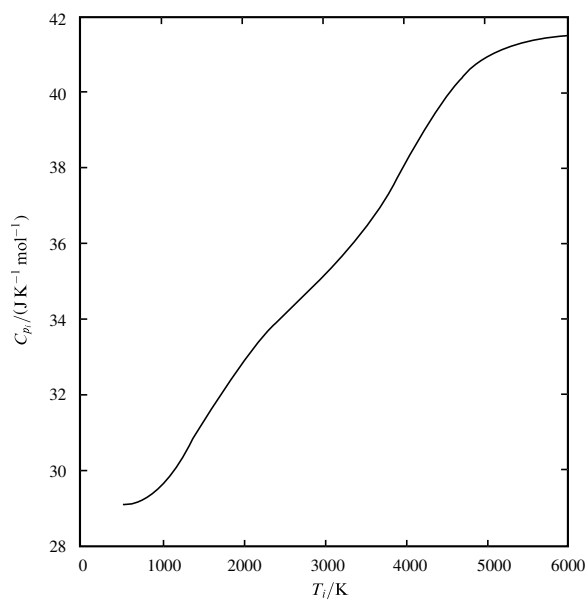$$C_{p_i} = C_{V_i} + R(1 + \alpha_i)$$

<div align="right">**Figure 20.6(b)**</div>

P20.14 $q = \dfrac{1}{1 - e^{-x}}, \quad x = \hbar\omega\beta = hc\tilde{\nu}\beta = \dfrac{\theta_V}{T}$ [Table 20.3]

$$U - U(0) = -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V = -N(1 - e^{-x})\frac{d}{d\beta}(1 - e^{-x})^{-1}$$

$$= \frac{N\hbar\omega e^{-x}}{1 - e^{-x}} = \boxed{\frac{N\hbar\omega}{e^x - 1}}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = -k\beta^2\frac{\partial U}{\partial \beta} = -k\beta^2\hbar\omega\frac{\partial U}{\partial x}$$

$$= k(\beta\hbar\omega)^2 N\left\{\frac{e^x}{(e^x - 1)^2}\right\} = \boxed{kN\left\{\frac{x^2 e^x}{(e^x - 1)^2}\right\}}$$

$$H - H(0) = U - U(0)[q \text{ is independent of } V] = \frac{N\hbar\omega e^{-x}}{1 - e^{-x}} = \boxed{\frac{N\hbar\omega}{e^x - 1}}$$

$$S = \frac{U - U(0)}{T} + nR\ln q = \frac{Nkxe^{-x}}{1 - e^{-x}} - Nk\ln(1 - e^{-x})$$

$$= \boxed{Nk\left(\frac{x}{e^x - 1} - \ln(1 - e^{-x})\right)}$$

$$A - A(0) = G - G(0) = -nRT\ln q$$

$$= \boxed{NkT\ln(1 - e^{-x})}$$

The functions are plotted in Fig. 20.7.

P20.15   **(a)** $\dfrac{N_J}{N} = \dfrac{g_J e^{-\varepsilon_J/kT}}{\sum_J g_J e^{-\varepsilon_J/kT}} = \dfrac{g_J e^{-\varepsilon_J/kT}}{q}$

For a linear molecule $g_J = 2J + 1$ and $\varepsilon_J = hcBJ(J + 1)$. Therefore,

$$N_J \propto (2J + 1)e^{-hcBJ(J+1)/kT}$$

(b) J_{max} occurs when $dn_J/dJ = 0$.

$$\frac{dN_J}{dJ} = \frac{N}{q}\frac{d}{dJ}\left\{(2J + 1)e^{-\left(\frac{hcBJ(J+1)}{kT}\right)}\right\} = 0$$

$$2 - (2J_{max} + 1)\left(\frac{hcB}{kT}\right)(2J_{max} + 1) = 0$$

$$2J_{max} + 1 = \left(\frac{2kT}{hcB}\right)^{1/2}$$

$$\boxed{J_{max} = \left(\frac{kT}{2hcB}\right)^{1/2} - \frac{1}{2}}$$

(c) $J_{max} \approx 3$ because the R branch $J = 3 \rightarrow 4$ transition has the least transmittance. Solving the previous equation for T provides the desired temperature estimate.
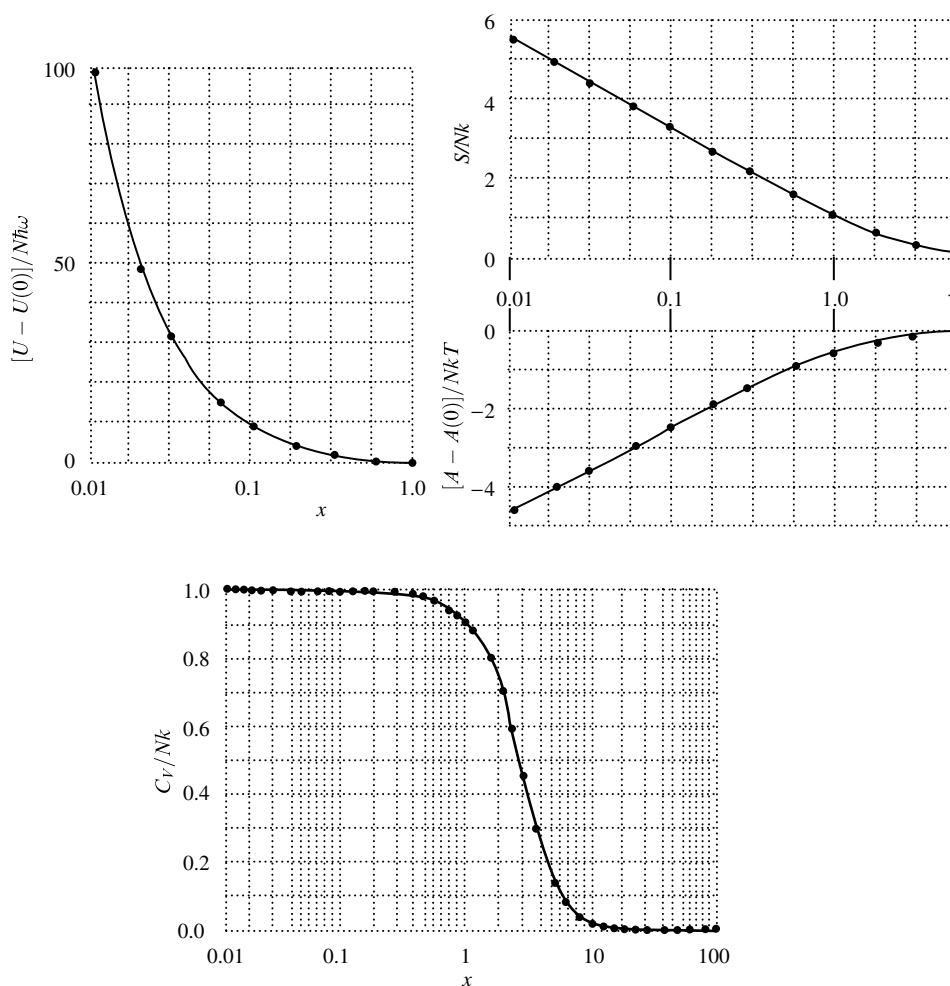
Figure 20.7

$$T \approx \frac{hcB}{2k}(2J_{max} + 1)^2$$

$$\approx \frac{(6.626 \times 10^{-34} \text{ J s}) \times (3.000 \times 10^8 \text{ m s}^{-1}) \times (10.593 \text{ cm}^{-1}) \times \left(\frac{10^2 \text{ cm}}{\text{m}}\right) \times (7)^2}{2(1.38066 \times 10^{-23} \text{ J K}^{-1})}$$

$$\boxed{T \approx 374 \text{ K}}$$

P20.17 All partition functions other than the electronic partition function are unaffected by a magnetic field; hence the relative change in K is the relative change in q^E.

$$q^E = \sum_{M_J} e^{-g\mu_B \beta \mathcal{B} M_J}, \quad M_J = -\tfrac{3}{2}, -\tfrac{1}{2}, +\tfrac{1}{2}, +\tfrac{3}{2}; \quad g = \tfrac{4}{3}$$

Since $g\mu_B \beta \mathcal{B} \ll 1$ for normally attainable fields,

$$q^E = \sum_{M_J} \left\{ 1 - g\mu_B \beta \mathcal{B} M_J + \frac{1}{2}(g\mu_B \beta \mathcal{B} M_J)^2 + \cdots \right\}$$

$$= 4 + \frac{1}{2}(g\mu_B \beta \mathcal{B})^2 \sum_{M_J} M_J^2 \left[\sum_{M_J} M_J = 0 \right] = 4 \left(1 + \frac{10}{9}(\mu_B \beta \mathcal{B})^2 \right) \quad \left[g = \frac{4}{3} \right]$$

Therefore, if K is the actual equilibrium constant and K^0 is its value when $\mathcal{B} = 0$, we write

$$\frac{K}{K^0} = \left(1 + \frac{10}{9}(\mu_B \beta \mathcal{B})^2 \right)^2 \approx 1 + \frac{20}{9}\mu_B^2 \beta^2 \mathcal{B}^2$$

For a shift of 1 per cent, we require

$$\frac{20}{9}\mu_B^2 \beta^2 \mathcal{B}^2 \approx 0.01, \quad \text{or} \quad \mu_B \beta \mathcal{B} \approx 0.067$$

Hence

$$\mathcal{B} \approx \frac{0.067 kT}{\mu_B} = \frac{(0.067) \times (1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (1000\,\text{K})}{9.274 \times 10^{-24}\,\text{J T}^{-1}} \approx \boxed{100\,\text{T}}$$

Solutions to applications

P20.20 The standard molar Gibbs energy is given by

$$G_m^{\ominus} - G_m^{\ominus}(0) = RT \ln \frac{q_m^{\ominus}}{N_A} \quad \text{where} \quad \frac{q_m^{\ominus}}{N_A} = \frac{q_{m,tr}^{\ominus}}{N_A} q^R q^V q^E$$

Translation: $\quad \dfrac{q_{m,tr}^{\ominus}}{N_A} = \dfrac{kT}{p^{\ominus}\Lambda^3} = 2.561 \times 10^{-2}(T/\text{K})^{5/2}(M/\text{g mol}^{-1})^{3/2}$

$$= (2.561 \times 10^{-2}) \times (2000)^{5/2} \times (38.90)^{3/2}$$

$$= 1.111 \times 10^9$$

Rotation of a linear molecule:

$$q^R = \frac{kT}{\sigma hcB} = \frac{0.6950}{\sigma} \times \frac{T/\text{K}}{B/\text{cm}^{-1}}$$

The rotational constant is

$$B = \frac{\hbar}{4\pi cI} = \frac{\hbar}{4\pi c m_{eff} R^2} \quad \text{where} \quad m_{eff} = \frac{m_B m_{Si}}{m_B + m_{Si}}$$

$$= \frac{(10.81) \times (28.09)}{10.81 + 28.09} \times \frac{10^{-3}\,\text{kg mol}^{-1}}{6.022 \times 10^{23}\,\text{mol}^{-1}}$$

$$m_{eff} = 1.296 \times 10^{-26}\,\text{kg}$$

$$B = \frac{1.0546 \times 10^{-34}\,\text{J s}}{4\pi(2.998 \times 10^{10}\,\text{cm s}^{-1}) \times (1.296 \times 10^{-26}\,\text{kg}) \times (190.5 \times 10^{-12}\,\text{m})^2} = 0.5952\,\text{cm}^{-1}$$

so $q^R = \dfrac{0.6950}{1} \times \dfrac{2000}{0.5952} = 2335$

Vibration: $\quad q^V = \dfrac{1}{1 - e^{-hc\tilde{v}/kT}} = \dfrac{1}{1 - \exp\left(\dfrac{-1.4388(\tilde{v}/\mathrm{cm}^{-1})}{T/\mathrm{K}}\right)} = \dfrac{1}{1 - \exp\left(\dfrac{-1.4388(772)}{2000}\right)}$

$$= 2.467$$

The Boltzmann factor for the lowest-lying electronic excited state is

$$\exp\left(\frac{-(1.4388)\times(8000)}{2000}\right) = 3.2 \times 10^{-3}$$

The degeneracy of the ground level is 4 (spin degeneracy = 4, orbital degeneracy = 1), and that of the excited level is also 4 (spin degeneracy = 2, orbital degeneracy = 2), so

$$q^E = 4(1 + 3.2 \times 10^{-3}) = 4.013$$

Putting it all together yields

$$\begin{aligned}
G_m^{\ominus} - G_m^{\ominus}(0) &= (8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}}) \times (2000\,\mathrm{K})\ln(1.111 \times 10^9) \times (2335) \\
&\quad \times (2.467) \times (4.013) \\
&= 5.135 \times 10^5\,\mathrm{J\,mol^{-1}} = \boxed{513.5\,\mathrm{kJ\,mol^{-1}}}
\end{aligned}$$

P20.22 The standard molar Gibbs energy is given by

$$G_m^{\ominus} - G_m^{\ominus}(0) = RT \ln \frac{q_m^{\ominus}}{N_A} \quad \text{where} \quad \frac{q_m^{\ominus}}{N_A} = \frac{q_{m,\mathrm{tr}}^{\ominus}}{N_A}q^R q^V q^E$$

First, at 10.00 K

Translation: $\quad \dfrac{q_{m,\mathrm{tr}}^{\ominus}}{N_A} = 2.561 \times 10^{-2}(T/\mathrm{K})^{5/2}(M/\mathrm{g\,mol^{-1}})^{3/2}$

$$= (2.561 \times 10^{-2}) \times (10.00)^{5/2} \times (36.033)^{3/2}$$

$$= 1752$$

Rotation of a nonlinear molecule:

$$q^R = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2} = \frac{1.0270}{\sigma} \times \frac{(T/\mathrm{K})^{3/2}}{(ABC/\mathrm{cm}^{-3})^{1/2}}$$

The rotational constants are

$$B = \frac{\hbar}{4\pi cI} \quad \text{so} \quad ABC = \left(\frac{\hbar}{4\pi c}\right)^3 \frac{1}{I_A I_B I_C},$$

$$ABC = \left(\frac{1.0546 \times 10^{-34}\,\mathrm{J\,s}}{4\pi(2.998 \times 10^{10}\,\mathrm{cm\,s^{-1}})}\right)^3$$

$$\times \frac{(10^{10}\,\mathrm{\mathring{A}\,m}^{-1})^6}{(39.340)\times(39.032)\times(0.3082)\times(\mathrm{u\,\mathring{A}^2})^3\times(1.66054\times10^{-27}\,\mathrm{kg\,u^{-1}})^3}$$

$$= 101.2\,\mathrm{cm}^{-3}$$

so $\quad q^R = \dfrac{1.0270}{2} \times \dfrac{(10.00)^{3/2}}{(101.2)^{1/2}} = 1.614$

Vibration: $q^V = \dfrac{1}{1 - e^{-hc\tilde{\nu}/kT}} = \dfrac{1}{1 - \exp\left(\dfrac{-1.4388(\tilde{\nu}/\text{cm}^{-1})}{T/\text{K}}\right)} = \dfrac{1}{1 - \exp\left(\dfrac{-1.4388(63.4)}{10.00}\right)}$

$= 1.0001$

Even the lowest-frequency mode has a vibrational partition function of 1; so the stiffer vibrations have q^V even closer to 1. The degeneracy of the electronic ground state is 1, so $q^E = 1$. Putting it all together yields

$$G_m^\ominus - G_m^\ominus(0) = (8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}) \times (10.00\,\text{K})\ln(1752) \times (1.614) \times (1) \times (1)$$

$$= \boxed{660.8\,\text{J mol}^{-1}}$$

Now at 1000 K

Translation: $\dfrac{q_{m,tr}^\ominus}{N_A} = (2.561 \times 10^{-2}) \times (1000)^{5/2} \times (36.033)^{3/2} = 1.752 \times 10^8$

Rotation: $q^R = \dfrac{1.0270}{2} \times \dfrac{(1000)^{3/2}}{(101.2)^{1/2}} = 1614$

Vibration: $q^{V(1)} = \dfrac{1}{1 - \exp\left(-\dfrac{(1.4388)\times(63.4)}{1000}\right)} = 11.47$

$q^{V(2)} = \dfrac{1}{1 - \exp\left(-\dfrac{(1.4388)\times(1224.5)}{1000}\right)} = 1.207$

$q^{V(3)} = \dfrac{1}{1 - \exp\left(-\dfrac{(1.4388)\times(2040)}{1000}\right)} = 1.056$

$q^V = (11.47) \times (1.207) \times (1.056) = 14.62$

Putting it all together yields

$$G_m^\ominus - G_m^\ominus(0) = (8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}) \times (1000\,\text{K}) \times \ln(1.752 \times 10^8) \times (1614)$$

$$\times (14.62) \times (1)$$

$$= 2.415 \times 10^5\,\text{J mol}^{-1} = \boxed{241.5\,\text{kJ mol}^{-1}}$$