Chapter 4 Calculation of Thermodynamic Properties

Energy

An average energy of one molecule

$$\langle \varepsilon \rangle = \frac{E}{N} = \frac{\sum\limits_n \varepsilon_n a_n}{N} = \sum_n \varepsilon_n \frac{a_n}{N}$$

ε_n: the level energy

a_n: the occupation number for the level

The Boltzmann distribution for a series of non-degenerate energy levels

$$\frac{a_n}{N}=\frac{e^{-\beta\varepsilon_n}}{q}$$

$$\langle\varepsilon\rangle=\sum_n \varepsilon_n P_n=\sum_n \varepsilon_n \frac{a_n}{N}=\frac{1}{q}\sum_n \varepsilon_n e^{-\beta\varepsilon_n};\quad -\frac{dq}{d\beta}=\sum_n \varepsilon_n e^{-\beta\varepsilon_n}$$

$$\therefore\langle\varepsilon\rangle=-\frac{1}{q}\frac{dq}{d\beta}=-\frac{d\ln q}{d\beta}$$

$$E=N\langle\varepsilon\rangle=-\frac{N}{q}\left(\frac{dq}{d\beta}\right)=-N\left(\frac{d\ln q}{d\beta}\right)$$

$$\beta=\frac{1}{kT}\ \rightarrow\ \frac{d\beta}{dT}=\frac{d}{dT}(kT)^{-1}=-\frac{1}{kT^2}$$

$$\therefore\langle\varepsilon\rangle=kT^2\left(\frac{d\ln q}{dT}\right)$$

$$E=NkT^2\left(\frac{d\ln q}{dT}\right)$$

Example:

Determine the total energy of an ensemble consisting of *N* particles that have only two energy levels separated by *hν*.

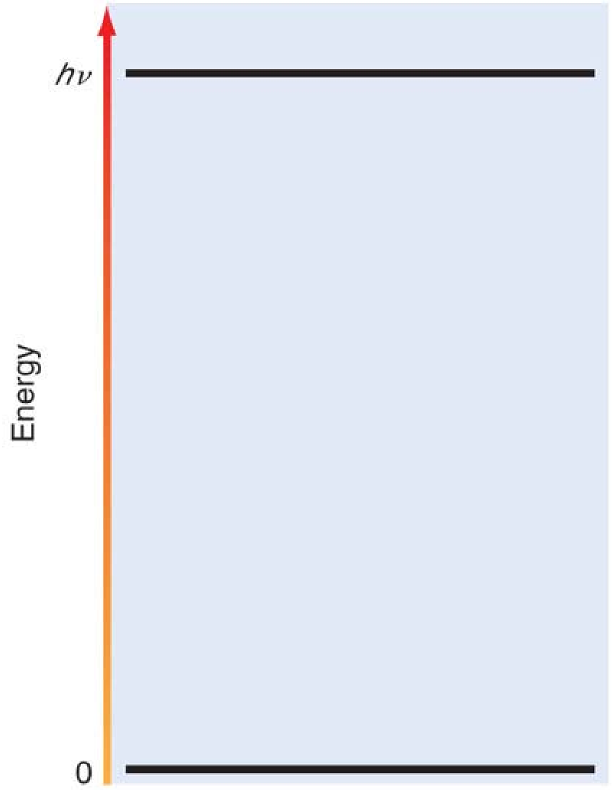


Figure 1. Depiction of the two-level system.

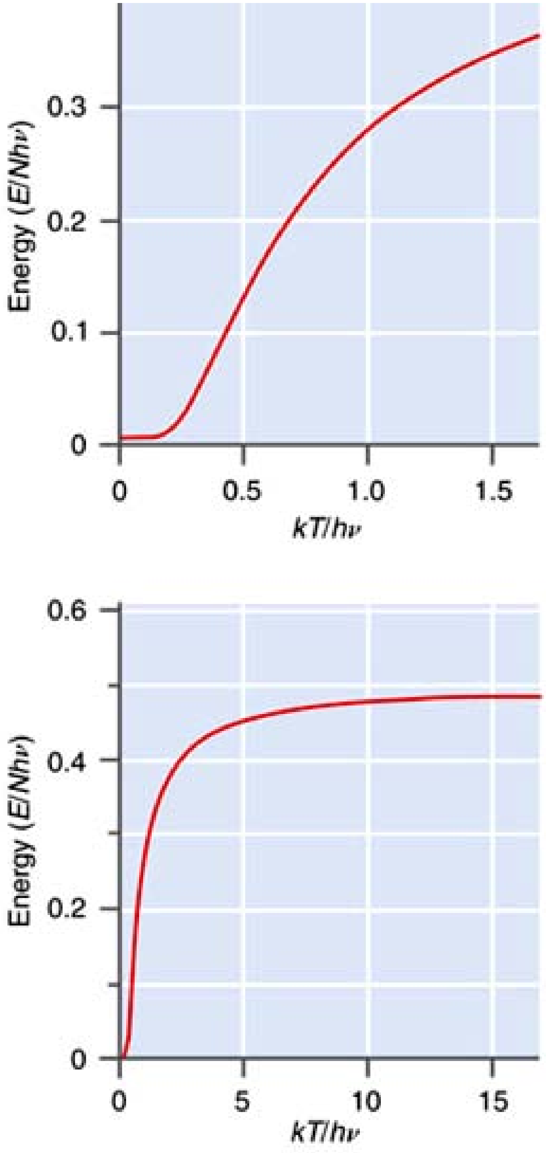


Figure 2. Total energy as a function of temperature is presented for an ensemble consisting of units that have two energy levels separated by an amount *hv*.

For the two-level system, the probability of occupying the excited energy level is

$$P_1 = \frac{a_1}{N} = \frac{e^{-\beta h\nu}}{q} = \frac{e^{-\beta h\nu}}{1+e^{-\beta h\nu}}$$

$$= \frac{1}{e^{\beta h\nu}+1}$$

At $T=0$, $P_1=0$

P_1 increases until $h\nu << kT$.

At high temperature, $P_1 \to 0.5$

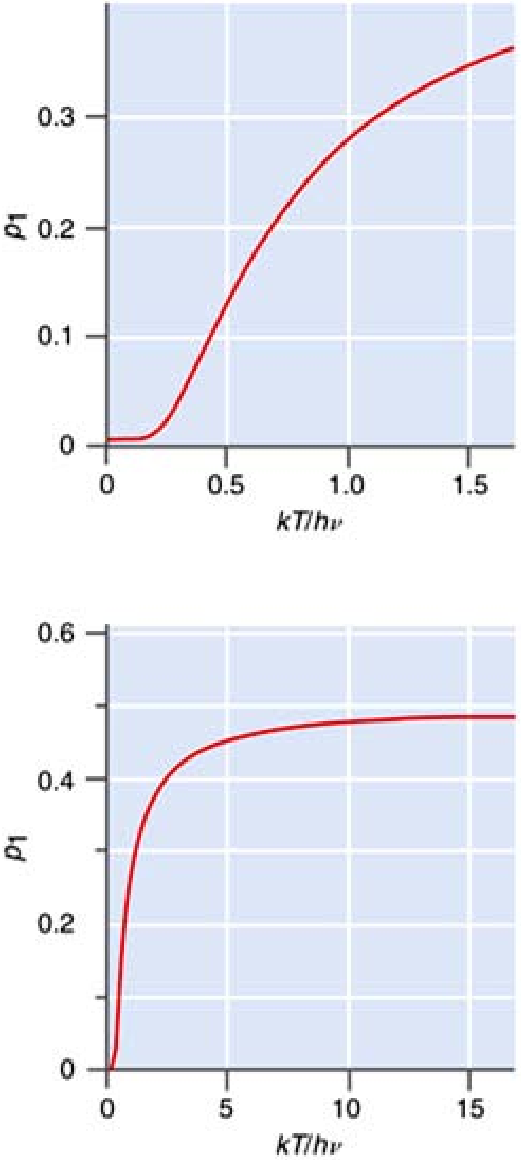


Figure 3. The probability of occupying the excited state in a two-level system is shown as a function of temperature.

Energy and the Canonical Partition Function

Canonical ensemble: *N, V, T* are held constant; No *p*-*V* work

$$\therefore U - U_o = q_V$$

$$Q = \frac{q^N}{N!}$$

$$\ln Q = \ln\left(\frac{q^N}{N!}\right) = N\ln q - \ln N!$$

$$\frac{d\ln Q}{d\beta} = \frac{d}{d\beta}(N\ln q) - \frac{d}{d\beta}(\ln N!)$$

$$= N\frac{d\ln q}{d\beta}$$

Since $\langle\varepsilon\rangle = -\frac{d\ln q}{d\beta}$, $\frac{d\ln Q}{d\beta} = -N\langle\varepsilon\rangle = -U$

$$\boldsymbol{U = -\left(\frac{d\ln Q}{d\beta}\right)_v}$$

Note: $E = U + pV$. At const *V*, $E = U$.

Example:

For an ensemble consisting of a mole of particles having two energy levels separated by $hv = 1\text{x}10^{-20}\ J$, at what temperature will the internal energy of this system equal 1.00 kJ?

Energy and Molecular Energetic Degree of Freedom

$$q_{tot} = q_t q_r q_v q_e$$

$$\begin{aligned}
U &= -\left(\frac{d\ln Q}{d\beta}\right)_V = -N\left(\frac{d\ln q}{d\beta}\right)_V = -N\left(\frac{d\ln q_t q_r q_v q_e}{d\beta}\right)_V \\
&= -N\left(\frac{d}{d\beta}(\ln q_t + \ln q_r + \ln q_v + \ln q_e)\right)_V \\
&= -N\left[\left(\frac{d\ln q_t}{d\beta}\right)_V + \left(\frac{d\ln q_r}{d\beta}\right)_V + \left(\frac{d\ln q_v}{d\beta}\right)_V + \left(\frac{d\ln q_e}{d\beta}\right)_V\right] \\
&= U_t + U_r + U_v + U_e
\end{aligned}$$

Translations

$$U_t = -\frac{N}{q_t}\left(\frac{dq_t}{d\beta}\right)_V \text{, where } q_t = \frac{V}{\Lambda^3}\ ,\ \Lambda^3 = \left(\frac{h^2\beta}{2\pi m}\right)^{\frac{3}{2}}.$$

$$\therefore U_t = -\frac{N}{q_t}\left(\frac{dq_t}{d\beta}\right)_V = -\frac{N\Lambda^3}{V}\left(\frac{d}{d\beta}\left(\frac{V}{\Lambda^3}\right)\right)$$

$$\Lambda^3 = \left(\frac{h^2\beta}{2\pi m}\right)^{\frac{3}{2}}$$

$$= -N\Lambda^3\left(\frac{d}{d\beta}\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}}\right)_V$$

$$= -N\Lambda^3\left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}}\left(\frac{d}{d\beta}\beta^{-\frac{3}{2}}\right)_V$$

$$= -N\Lambda^3\left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}}\left(-\frac{3}{2}\beta^{-\frac{5}{2}}\right)$$

$$= \frac{3}{2}N\Lambda^3\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}}\beta^{-1}$$

$$= \frac{3}{2}N\beta^{-1}$$

$$\therefore U_t = \frac{3}{2}NkT = \frac{3}{2}nRT$$

Rotations

For a diatomic molecule in the high-temperature limit within the rigid rotor approximation,

$$q_r = \frac{1}{\sigma\beta hcB}$$

$$U_r = -\frac{N}{q_r}\left(\frac{dq_r}{d\beta}\right)_V = -N\sigma\beta hcB\left(\frac{d}{d\beta}\frac{1}{\sigma\beta hcB}\right)_V = -N\beta\left(\frac{d}{d\beta}\beta^{-1}\right)_V$$

$$= -N\beta(-\beta^{-2}) = N\beta^{-1}$$

$$\therefore U_r = NkT = nRT$$

The concept of equipartition

$U_r = nRT$ (linear polyatomic)

$U_r = \frac{3}{2}RT$ (non-linear polyatomic)

Vibrations

$$q_v = \frac{1}{1-e^{-\beta hc\tilde{v}}}$$

$$U_v = -\frac{N}{q_v}\left(\frac{dq_v}{d\beta}\right)_V = -N\left(1-e^{-\beta hc\tilde{v}}\right)\left(\frac{d}{d\beta}\left(\frac{1}{1-e^{-\beta hc\tilde{v}}}\right)\right)_V$$

$$= -N\left(1-e^{-\beta hc\tilde{v}}\right)\left(-hc\tilde{v}e^{-\beta hc\tilde{v}}\right)\left(1-e^{-\beta hc\tilde{v}}\right)^{-2}$$

$$= \frac{Nhc\tilde{v}e^{-\beta hc\tilde{v}}}{\left(1-e^{-\beta hc\tilde{v}}\right)}$$

$$= \frac{Nhc\tilde{v}}{e^{\beta hc\tilde{v}}-1}$$

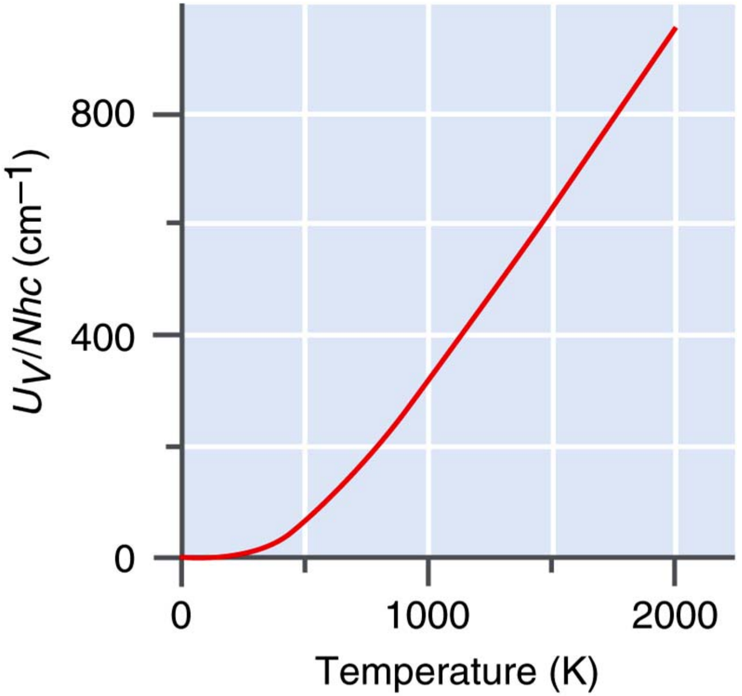


Figure 4. The variation in average vibrational energy as a function of temperature where $\tilde{\nu} = 1000 \text{ cm}^{-1}$.

For the high-temperature limit, $kT \gg hc\tilde{\nu}$, i.e., $T \gg \theta_v$.

$$e^x = 1 + x + \frac{x^2}{2} + \cdots \cong 1 + x \qquad x \ll 1$$

$$x = \beta hc\tilde{\nu} = \frac{hc\tilde{\nu}}{kT}, \quad kT \gg hc\tilde{\nu} \qquad\qquad U_v = \frac{Nhc\tilde{\nu}}{e^{\beta hc\tilde{\nu}} - 1}$$

$$U_v = \frac{Nhc\tilde{\nu}}{e^{\beta hc\tilde{\nu}} - 1} = \frac{Nhc\tilde{\nu}}{(1 + \beta hc\tilde{\nu}) - 1} = \frac{Nhc\tilde{\nu}}{\beta hc\tilde{\nu}} = \frac{N}{\beta} = NkT = nRT$$

$$\theta_v = \frac{hc\tilde{\nu}}{k}$$

The high-temperature limit is applicable when $T \geq 10\,\theta_v$.

Review

For a diatomic molecule,

$$\begin{aligned} U_{tot} &= U_t + U_r + U_v + U_e \\ &= \frac{3}{2}NkT + NkT + \frac{Nhc\tilde{\nu}}{e^{\beta hc\tilde{\nu}} - 1} + 0 \\ &= \frac{5}{2}NkT + \frac{Nhc\tilde{\nu}}{e^{\beta hc\tilde{\nu}} - 1} \end{aligned}$$

Heat Capacity

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

Example:

Determine the heat capacity for an ensemble consisting of units that have only two energy levels separated by an arbitrary amount of energy $h\nu$.

Translational Heat Capacity

For an ideal gas,

$$U_t = \frac{3}{2} NkT$$

$$C_{V,t} = \left(\frac{dU_t}{dT} \right)_V = \frac{3}{2} Nk$$

Rotational Heat Capacity

$U_r = NkT$ (linear)

$U_r = \frac{3}{2} NkT$ (non-linear)

$C_{V,r} = Nk$ (linear)

$C_{V,r} = \frac{3}{2} Nk$ (non-linear)

Vibrational Heat Capacity

$$U_v = \frac{Nhc\tilde{\nu}}{e^{\beta hc\tilde{\nu}} - 1}$$

$$\therefore C_{V,v} = \left(\frac{dU_v}{dT}\right)_V = -k\beta^2\left(\frac{dU_v}{d\beta}\right)_V$$

$$= -Nk\beta^2 hc\tilde{\nu}\left(\frac{d}{d\beta}\left(\frac{1}{e^{\beta hc\tilde{\nu}} - 1}\right)\right)_V$$

$$= -Nk\beta^2 hc\tilde{\nu}\left(-\frac{hc\tilde{\nu}e^{\beta hc\tilde{\nu}}}{\left(e^{\beta hc\tilde{\nu}} - 1\right)^2}\right)_V$$

$$= Nk\beta^2 \left(hc\tilde{\nu}\right)^2 \frac{e^{\beta hc\tilde{\nu}}}{\left(e^{\beta hc\tilde{\nu}} - 1\right)^2}$$

$$= Nk\left(\frac{\theta_v}{T}\right)^2 \frac{e^{\theta_v/T}}{\left(e^{\theta_v/T} - 1\right)^2}$$

For a polyatomic molecule, it has 3*N*-6 or 3*N*-5 vibrational dergee of freedom.

$$\left(C_{V,v}\right)_{tot} = \sum_{m=1}^{3N-6 \text{ or } 3N-5} \left(C_{V,v}\right)_m$$

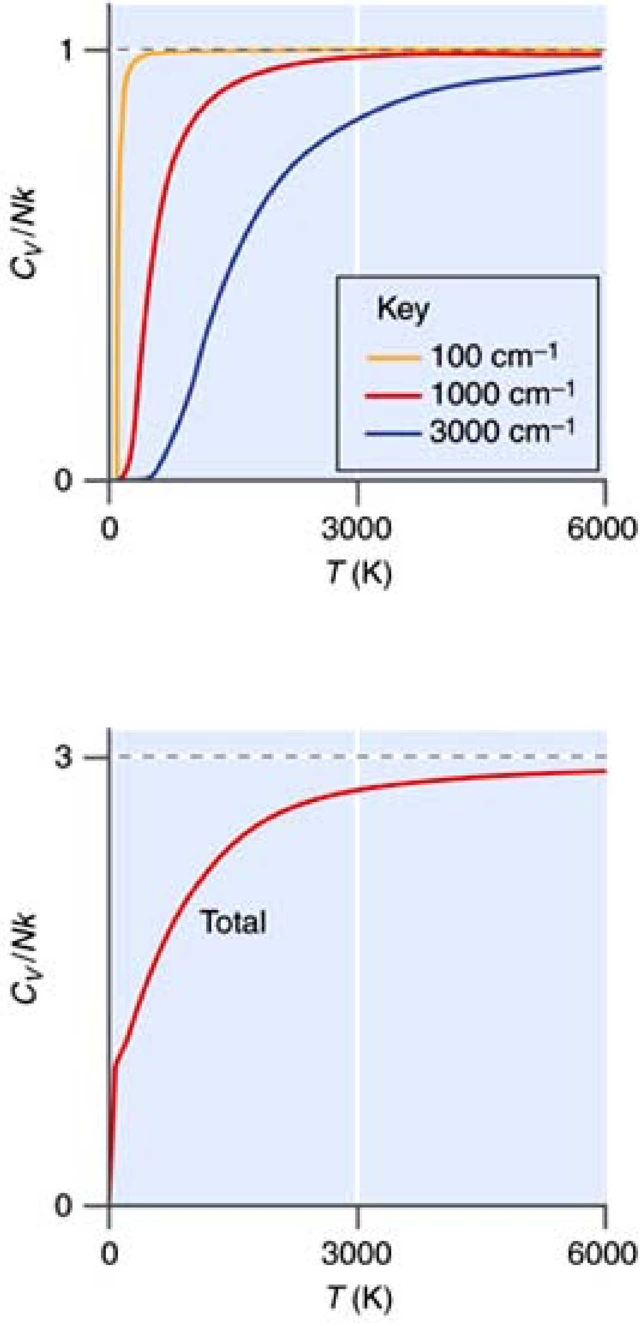


Figure 5. Evolution in the vibrational contribution to C_V as a function of temperature. Calculations are for a molecule with three vibrational degrees of freedom as indicated in the top panel. Contribution for each vibrational mode (top) and the total vibrational contribution (bottom).

Review

For a diatomic molecule,

$$C_{V,tot} = C_{V,t} + C_{V,r} + C_{V,v}$$

$$= \frac{3}{2}Nk + Nk + Nk\beta^2 (hc\tilde{\nu})^2 \frac{e^{\beta hc\tilde{\nu}}}{\left(e^{\beta hc\tilde{\nu}} - 1\right)^2}$$

$$= \frac{5}{2}Nk + Nk\beta^2 (hc\tilde{\nu})^2 \frac{e^{\beta hc\tilde{\nu}}}{\left(e^{\beta hc\tilde{\nu}} - 1\right)^2}$$

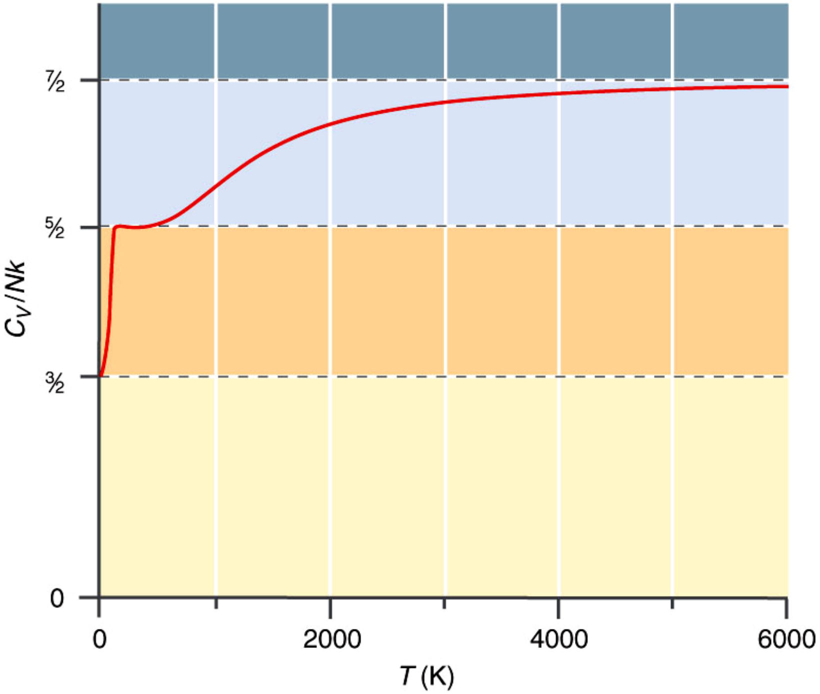


Figure 6. The constant volume heat capacity for gaseous HCl as a function of temperature. The contributions of translational (yellow), rotational (orange), and vibrational (light blue) degrees of freedom to the heat capacity are shown.

The Einstein Solid

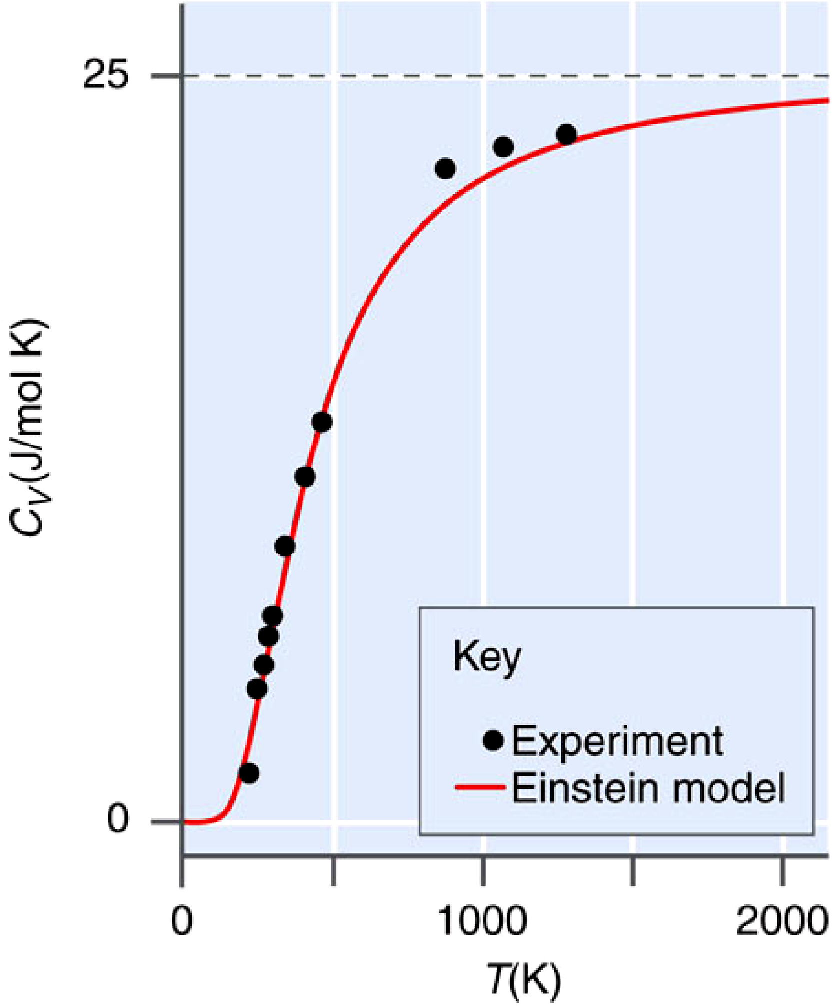
The Einstein solid model was developed to describe the thermodynamic properties of atomic crystalline systems.

1. All of the harmonic oscillators are assumed to be separable.
2. The harmonic oscillators are assumed to be isoenergetic.

For a crystal containing N atoms, there are $3N$ vibrational degrees of freedom

$$C_{V,tot} = 3Nk\left(\frac{\theta_v}{T}\right)^2 \frac{e^{\theta_v/T}}{\left(e^{\theta_v/T}-1\right)^2}$$

The total heat capacity is identical to that of a collection of $3N$ harmonic oscillators.



⟶ the Dulong and Petit Law

Figure 7. Comparison of C_V for diamond to the theoretical prediction of the Einstein solid model. The classical limit of 24.91 *J/mol K* is shown as the dashed line.

Note that the model predicts that the heat capacity should reach a limiting value of 24.91 *J/mol K* or 3*R* at high temperature.
This limiting law is known as the Dulong and Petit Law, and represents the high-temperature or classical prediction for the heat capacity of such systems.

A plot of C_V versus T/θ_v can describe the variation in heat capacity for all solids.

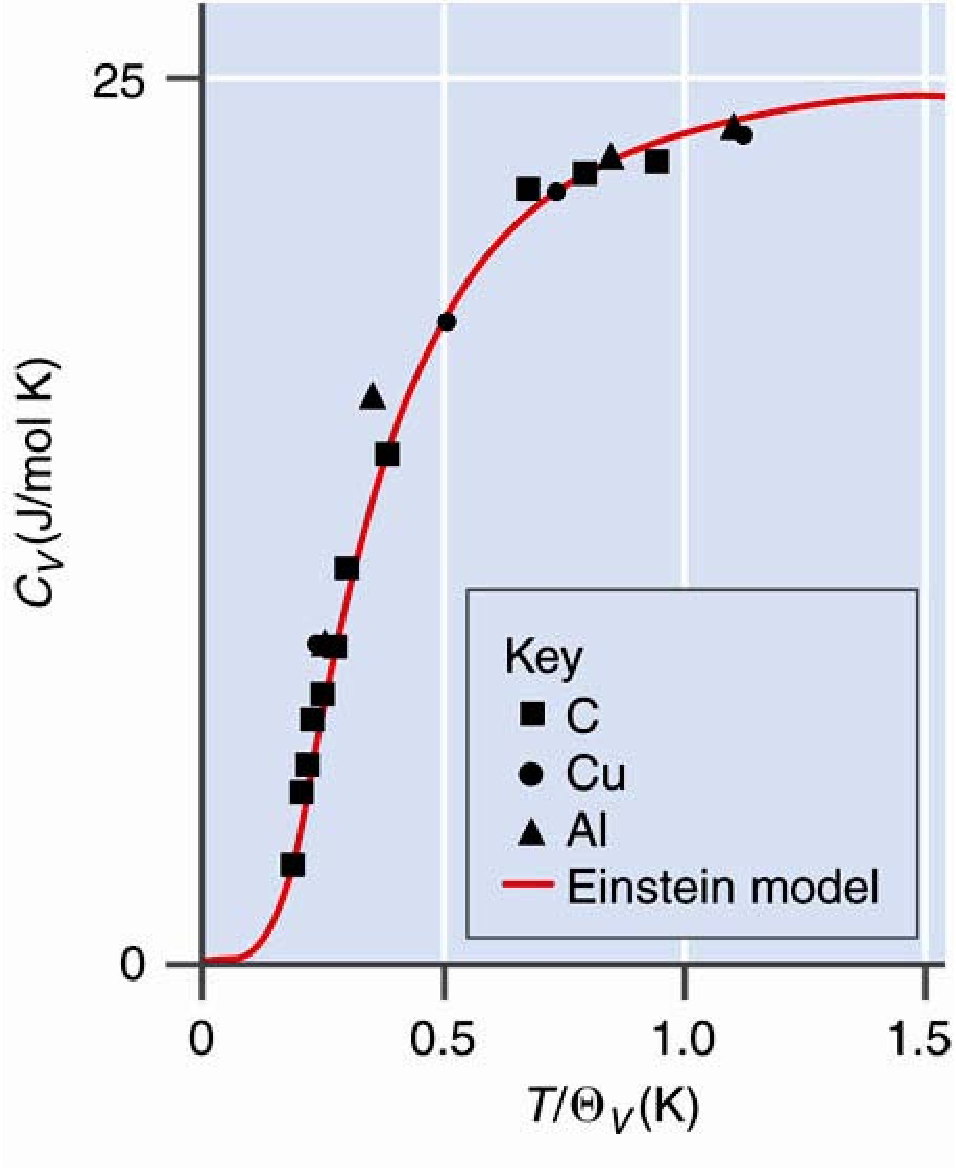
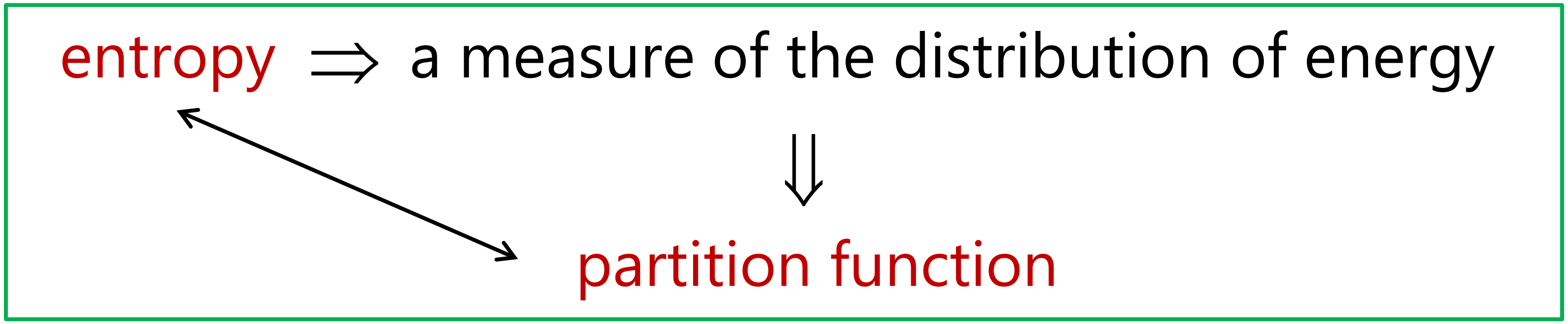


Figure 8. Comparison of C_V versus T/Θ_v for C, Cu, and Al.

Entropy



entropy ⇒ a measure of the distribution of energy

⇓

partition function

$$U = U(0) + \sum_n \varepsilon_n a_n$$

$$dU = dU(0) + \sum_n a_n d\varepsilon_n + \sum_n \varepsilon_n da_n$$

$$dU = \sum_n \varepsilon_n da_n$$ ← at constant volume ($d\varepsilon_n$=0)

$$dU = dq_{rev} = TdS$$

$$\therefore dS = \frac{dU}{T} = k\beta \sum_n \varepsilon_n da_n$$

$$\beta\varepsilon_n = \frac{\partial \ln W}{\partial a_n} + \alpha \qquad \left(\leftarrow \frac{\partial \ln W}{\partial a_n} + \alpha - \beta\varepsilon_n = 0 \right)$$

$$\therefore dS = k\sum_n \left(\frac{\partial \ln W}{\partial a_n}\right) da_n + k\alpha \sum_n da_n$$

$$= k\sum_n \left(\frac{\partial \ln W}{\partial a_n}\right) da_n = k\left(d\ln W\right)$$

$$\left(\leftarrow \sum_n da_n = 0,\ \text{ i.e., the number of molecules is constant}\right)$$

$\therefore S = k\ln W$ the Boltzmann formula

$$S = k\ln\left[\frac{N!}{\prod_n a_n!}\right] = k\ln N! - k\ln\prod_n a_n!$$

$$= k\ln N! - k\sum_n \ln a_n! = k(N\ln N - N) - k\sum_n\left(a_n \ln a_n - a_n\right)$$

$$= k(N\ln N - \sum_n a_n \ln a_n) \qquad \left(\leftarrow \sum a_n = N\right)$$

$$= k\left(\sum_n a_n \ln N - \sum_n a_n \ln a_n\right)$$

$$= -k \sum_n a_n \ln \frac{a_n}{N}$$

$$= -k \sum_n a_n \ln P_n$$

where P_n is the probability of occupying energy level *n*.

$$\ln P_n = \ln\left(\frac{e^{-\beta\varepsilon_n}}{q}\right) = -\beta\varepsilon_n - \ln q$$

$$\therefore S = -k \sum_n a_n \ln P_n$$

$$= -k\left(\sum_n a_n \left(-\beta\varepsilon_n - \ln q\right)\right)$$

$$= k\beta \sum_n a_n\varepsilon_n + k\sum_n a_n \ln q$$

$$= k\beta E + kN \ln q$$

$$= \frac{E}{T} + k \ln q^{N}$$

$$= \frac{E}{T} + k \ln Q$$

$$= \frac{U}{T} + k \ln Q$$

$$U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V} = kT^{2}\left(\frac{d \ln Q}{dT}\right)_{V}$$

$$\therefore S = \frac{U}{T} + k \ln Q = kT\left(\frac{d \ln Q}{dT}\right)_{V} + k \ln Q$$

$$= \left(\frac{d}{dT}\left(kT \ln Q\right)\right)_{V}$$

Entropy of an Ideal Monatomic Gas

$$S = \left(\frac{d}{dT}\left(kT\ln Q\right)\right)_V = \frac{U}{T} + k\ln Q$$

$$= \frac{1}{T}\left(\frac{3}{2}NkT\right) + k\ln\frac{q_{trans}^N}{N!} \qquad \left(\leftarrow U = \frac{3}{2}NkT \text{ for monoatomic gas}\right)$$

$$= \frac{3}{2}Nk + Nk\ln q_{trans} - k\left(N\ln N - N\right)$$

$$= \frac{5}{2}Nk + Nk\ln q_{trans} - Nk\ln N$$

$$= \frac{5}{2}Nk + Nk\ln\frac{V}{\Lambda^3} - Nk\ln N$$

$$= \frac{5}{2}Nk + Nk\ln V - Nk\ln\Lambda^3 - Nk\ln N$$

$$= \frac{5}{2}Nk + Nk\ln V - Nk\ln\left(\frac{h^2}{2\pi mkT}\right)^{3/2} - Nk\ln N$$

$$= \frac{5}{2} Nk + Nk \ln V + \frac{3}{2} Nk \ln T - Nk \ln \left(\frac{N^{2/3} h^2}{2\pi mk} \right)^{3/2}$$

$$= \frac{5}{2} nR + nR \ln V + \frac{3}{2} nR \ln T - nR \ln \left(\frac{n^{2/3} N_A{}^{2/3} h^2}{2\pi mk} \right)^{3/2}$$

The Sackur-Tetrode Equation

$$\therefore S = nR \ln \left[\frac{V e^{\frac{5}{2}}}{n N_A \Lambda^3} \right] = nR \ln \left[\frac{R T e^{\frac{5}{2}}}{\Lambda^3 N_A p} \right] \qquad \text{where } \Lambda^3 = \left(\frac{h^2}{2\pi mkT} \right)^{\frac{3}{2}}$$

$V_1 \rightarrow V_2$ for an ideal monatomic gas

$$\Delta S = S_{final} - S_{initial} = nR \ln \frac{V_2}{V_1}$$

$\because$ The second term of the Sackur-Tetrode equation depends only on volume while the other terms are unchanged.

$T_1 \rightarrow T_2$ $\Delta V = 0$

$$\Delta S = S_{final} - S_{initial} = \frac{3}{2} nR \ln \frac{T_2}{T_1} = nC_V \ln \frac{T_2}{T_1}$$

Example:

Determine the standard molar entropy of Ne and Kr under standard thermodynamic conditions (298 K, V_m= 24.4 l = 0.0244 m^3).

Residual Entropy

For CO, at thermodynamic standard temperature and pressure

$$S_{\mathrm{cal}} = 197.9 \quad J/mol \cdot K$$

$$S_{\mathrm{exp}} = 193.3 \quad J/mol \cdot K$$

$$S_{\mathrm{cal}} - S_{\mathrm{exp}} = 4.6 \quad J/mol \cdot K = \text{residual entropy}$$

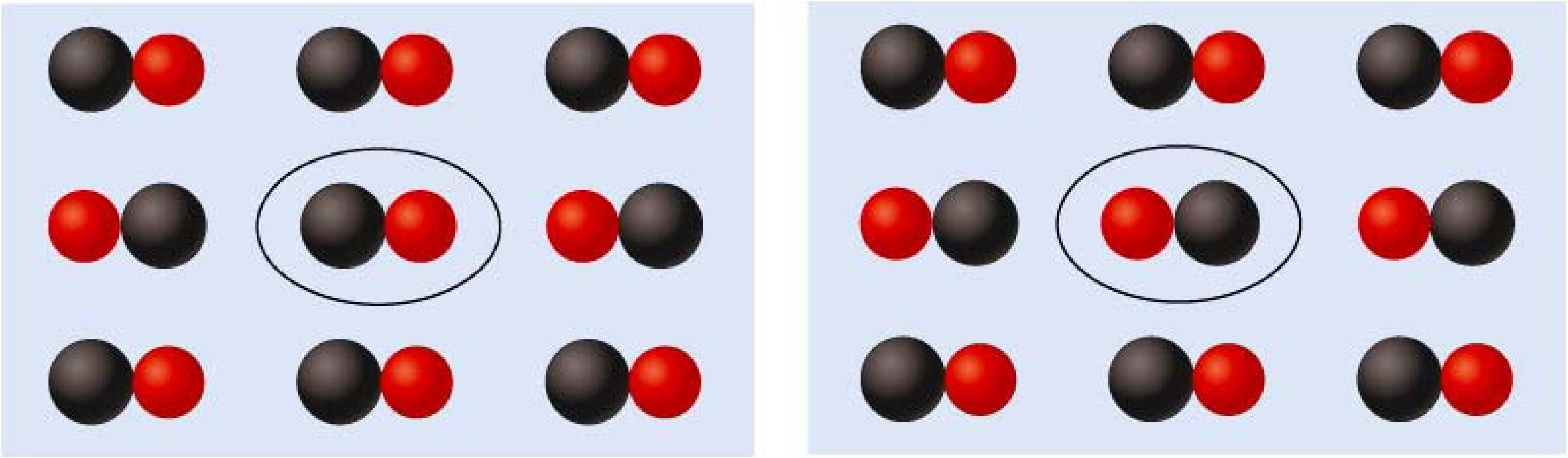


Figure 9. The origin of residual entropy for CO. Each CO molecule in the solid can have one of two possible orientations as illustrated by the central CO. Each CO will have two possible directions such that the total number of arrangements possible is 2^N where N is the number of CO molecules.

Because each CO molecule can assume one of two possible orientations, the entropy associated with this orientational order is

$$S = k\ln W = k\ln 2^N = Nk\ln 2 = nR\ln 2$$

For 1 mol, $S = R\ln 2 = 5.76 \ \ J/mol\cdot K$

Note: The third law of thermodynamics states that the entropy of a pure and crystalline substance is zero at 0 K.

Other Thermodynamic Functions

$$H = U + pV$$

$$A = U - TS$$

$$G = H - TS$$

Helmholtz Energy

$$A = U - TS = U - T\left(\frac{U}{T} + k\ln Q\right) \qquad \left(\leftarrow S = \frac{U}{T} + k\ln Q\right)$$

$$= -kT\ln Q$$

$$p = -\left(\frac{\partial A}{\partial V}\right)_T$$

$$= -\left(\frac{\partial\left(-kT\ln Q\right)}{\partial V}\right)_T$$

$$= kT\left(\frac{\partial}{\partial V}\ln Q\right)_T$$

$$Q = \frac{q^N}{N!}$$

$$p = kT\left(\frac{\partial}{\partial V}\ln\frac{q^N}{N!}\right)_T$$

$$= kT\left(\frac{\partial}{\partial V}\ln q^{N} - \frac{\partial}{\partial V}\ln N!\right)_T$$

$$= kT\left(\frac{\partial}{\partial V}\ln q^{N}\right)_T$$

$$= NkT\left(\frac{\partial}{\partial V}\ln q\right)_T$$

For a monatomic gas,

$$q = \frac{V}{\Lambda^3}$$

$$\therefore\ p = NkT\left(\frac{\partial}{\partial V}\ln\frac{V}{\Lambda^3}\right)_T$$

$$= NkT\left(\frac{\partial}{\partial V}\ln V - \frac{\partial}{\partial V}\ln\Lambda^3\right)_T$$

$$= NkT\left(\frac{\partial}{\partial V}\ln V\right)_T$$

$$= \frac{NkT}{V} = \frac{nRT}{V}$$ (← ideal gas law)

Enthalpy

$$H = U + pV$$

$$= -\left(\frac{\partial}{\partial\beta}\ln Q\right)_V + V\left(-\frac{\partial A}{\partial V}\right)_T \qquad \left(\leftarrow p = -\left(\frac{\partial A}{\partial V}\right)_T\right)$$

$$= -\left(\frac{\partial}{\partial\beta}\ln Q\right)_V + V\left(-\frac{\partial(-kT\ln Q)}{\partial V}\right)_T \qquad (\leftarrow A = -kT\ln Q)$$

$$= kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V + VkT\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

$$= T\left[kT\left(\frac{\partial \ln Q}{\partial T}\right)_V + Vk\left(\frac{\partial \ln Q}{\partial V}\right)_T\right]$$

Gibbs Energy

$$G = A + pV$$

$$= -kT\ln Q + VkT\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

$$= -kT\left[\ln Q - V\left(\frac{\partial \ln Q}{\partial V}\right)_T\right]$$

For an ideal gas,

$$G = A + pV$$

$$= -kT\ln Q + NkT$$

$$= -kT\ln\left(\frac{q^N}{N!}\right) + NkT$$

$$= -kT\ln q^N + kT\ln N! + NkT$$

$$= -NkT\ln q + kT(N\ln N - N) + NkT$$

$$= -NkT\ln q + NkT\ln N$$

$$= -NkT\ln\left(\frac{q}{N}\right) = -nRT\ln\left(\frac{q}{N}\right)$$

Example:

Calculate the Gibbs energy for 1 *mol* of Ar at 298.15 *K* and standard pressure (10^5 *Pa*), assuming that the gas demonstrates ideal behavior.

Chemical Equilibrium

For the reaction $aA + bB = cC + dD$,

$$\Delta G^0 = cG_C^0 + dG_D^0 - aG_A^0 - bG_B^0$$

$$\Delta G^0 = -RT\ln K$$

$$\Delta G^0 = c\left(-RT\ln\left(\frac{q_C^0}{N}\right)\right) + d\left(-RT\ln\left(\frac{q_D^0}{N}\right)\right) - a\left(-RT\ln\left(\frac{q_A^0}{N}\right)\right) - b\left(-RT\ln\left(\frac{q_B^0}{N}\right)\right)$$

$$= -RT\left(\ln\left(\frac{q_C^0}{N}\right)^c + \ln\left(\frac{q_D^0}{N}\right)^d - \ln\left(\frac{q_A^0}{N}\right)^a - \ln\left(\frac{q_B^0}{N}\right)^b\right)$$

$$= -RT\ln\left[\frac{\left(\frac{q_C^0}{N}\right)^c\left(\frac{q_D^0}{N}\right)^d}{\left(\frac{q_A^0}{N}\right)^a\left(\frac{q_B^0}{N}\right)^b}\right]$$

$$\therefore K_p = \left[\frac{\left(\frac{q_C^0}{N}\right)^c \left(\frac{q_D^0}{N}\right)^d}{\left(\frac{q_A^0}{N}\right)^a \left(\frac{q_B^0}{N}\right)^b} \right]$$

The vibrational and electronic ground state are not equivalent for all species, since the presence of a bond between the two atoms in the molecule lowers the energy of the molecule relative to the separated atomic fragments.

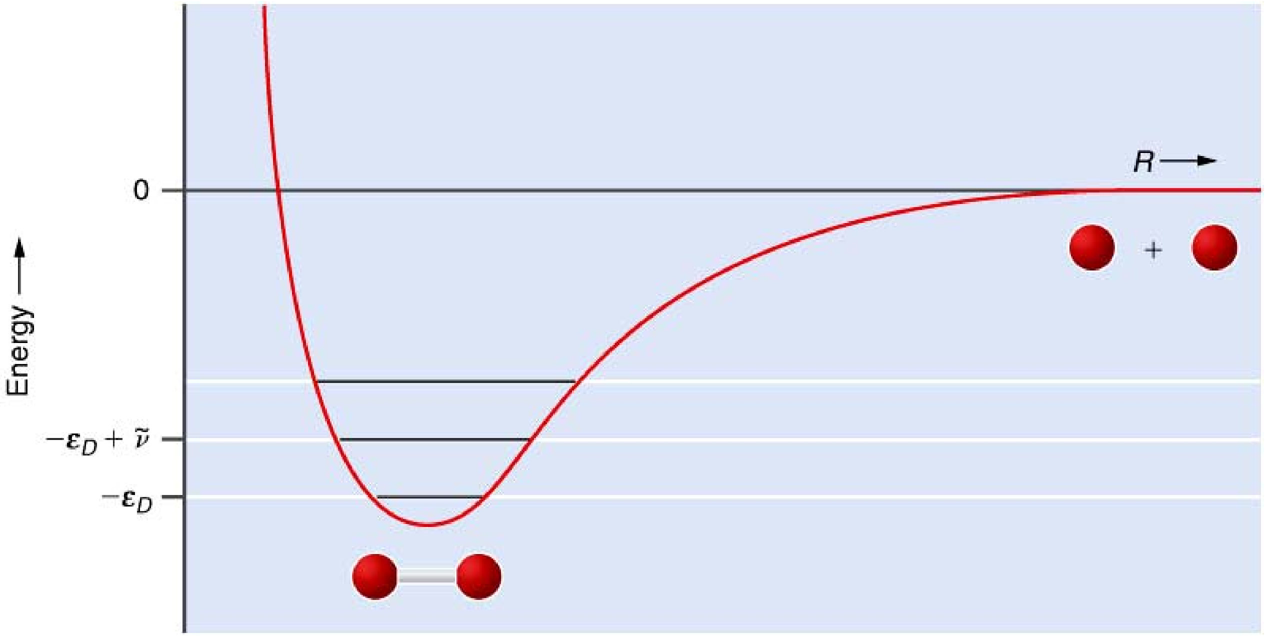


Figure 10. The ground-state potential energy curve for a diatomic molecule.

Because the energy of the atomic fragments is defined as zero, the ground vibrational state is lower than zero by an amount equal to the dissociation energy of the molecule, ε_D.

$$q_v{}' = \sum_n e^{-\beta\varepsilon_n} = e^{-\beta(-\varepsilon_D)} + e^{-\beta(-\varepsilon_D + hc\tilde{v})} + e^{-\beta(-\varepsilon_D + 2hc\tilde{v})} + \cdots$$

$$= e^{\beta\varepsilon_D}(1 + e^{-\beta hc\tilde{v}} + e^{-2\beta hc\tilde{v}} + \cdots)$$

$$= e^{\beta\varepsilon_D} q_v$$

$$\therefore K_p = \frac{\left(\frac{q_C^0}{N}\right)^c \left(\frac{q_D^0}{N}\right)^d}{\left(\frac{q_A^0}{N}\right)^a \left(\frac{q_B^0}{N}\right)^b} e^{\beta(c\varepsilon_C + d\varepsilon_D - a\varepsilon_A - b\varepsilon_B)}$$

$$= \frac{\left(\frac{q_C^0}{N}\right)^c \left(\frac{q_D^0}{N}\right)^d}{\left(\frac{q_A^0}{N}\right)^a \left(\frac{q_B^0}{N}\right)^b} e^{-\beta\Delta\varepsilon}$$

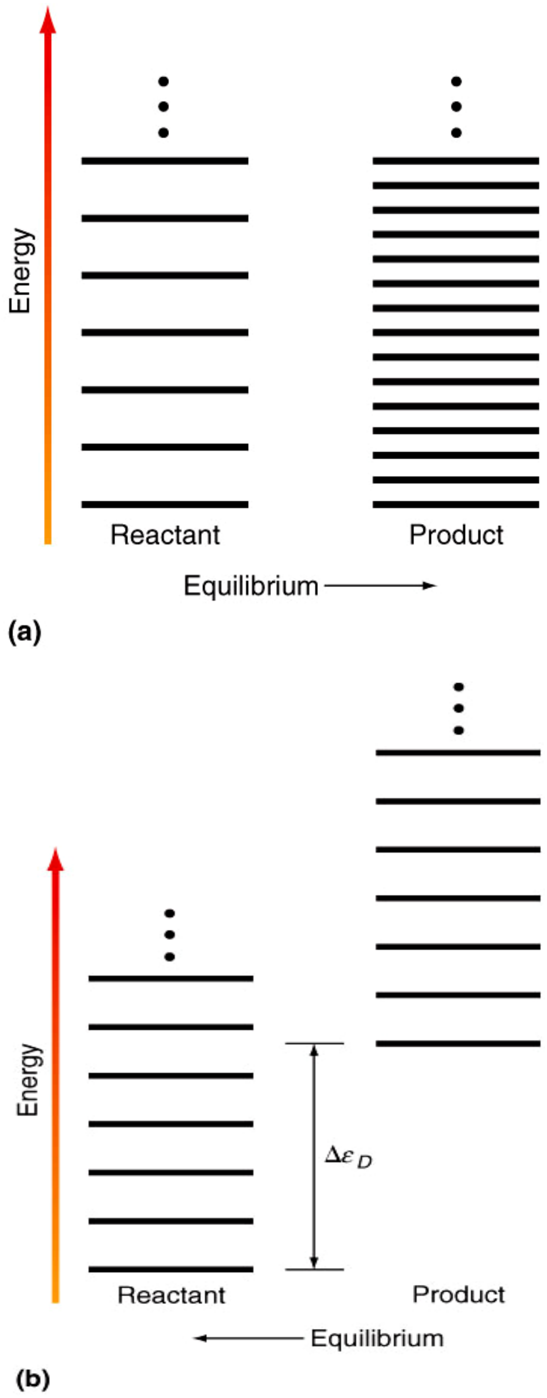


Figure 11. The statistical interpretation of equilibrium. (a) Reactant and product species having equal ground-state energies are depicted. However, the energy spacings of the product are less than the reactant such that more product states are available at a given temperature. Therefore, equilibrium will lie with the product. (b) Reactant and product species having equal state spacings are depicted. In this case, the product states are higher in energy than those of the reactant such that equilibrium lies with the reactant.

Example:

What is the general form of the equilibrium constant for the dissociation of a diatomic molecule?

$$X_2(g) \rightleftharpoons 2X(g)$$

Summary

$$q_{total} = q_t q_r q_v q_e$$

$$q_t = \frac{V}{\Lambda^3} \quad \text{where } \Lambda = \left(\frac{h^2\beta}{2\pi m}\right)^{1/2}$$

$$q_r = \frac{1}{\sigma\beta hcB} \quad \text{where } B = \frac{h}{8\pi^2 cI};\ I = \mu r^2;\ \mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{for diatomic}$$

$$q_r = \frac{\sqrt{\pi}}{\sigma}\left(\frac{1}{\beta hcB_A}\right)^{1/2}\left(\frac{1}{\beta hcB_B}\right)^{1/2}\left(\frac{1}{\beta hcB_C}\right)^{1/2} \quad \text{for non-linear polyatomic}$$

$$q_v = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}}$$

$$(q_v)_{total} = \sum_{i=1}^{3N-5 \text{ or } 3N-6} (q_v)_i$$

$$Q = q^N \quad \text{for distinguishable}$$

$$Q = \frac{q^N}{N!} \quad \text{for indistinguishable}$$

Canonical ensemble

$$U = -\left(\frac{d\ln Q}{d\beta}\right)_V$$

$$S = \left(\frac{d}{dT}(kT\ln Q)\right)_V$$

$$A = -kT\ln Q$$

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

$$G = -kT\left[\ln Q - V\left(\frac{\partial \ln Q}{\partial V}\right)_T\right]$$

$$\mu = -kT\left(\frac{\partial \ln Q}{\partial N}\right)_{V,T}$$