

Topic 4G - The Molecular Interpretation of Entropy

Statistical vs. Thermodynamic Entropy:

$$S = k_B \ln W$$

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$$

$$\Delta S = nC_v \ln \left(\frac{T_2}{T_1} \right) = n \times \frac{3}{2} R \ln \left(\frac{T_2}{T_1} \right) = nR \ln \left(\frac{T_2}{T_1} \right)^{3/2}$$

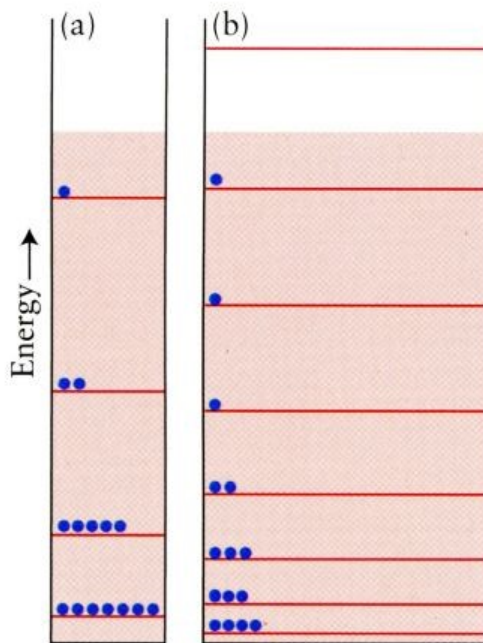


FIGURE 4G.4 (a) The energy levels of a particle in a box at $T > 0$. (b) The levels become closer together as the width of the box is increased. As a result, the number of levels accessible to the particles in the box at a given temperature increases, and the entropy of the system increases accordingly. The tinted band shows the range of thermally accessible levels. The change from part (a) to part (b) is a model of the isothermal expansion of an ideal gas. The total energy of the particles is the same in each case; only the distribution of energy levels differs.

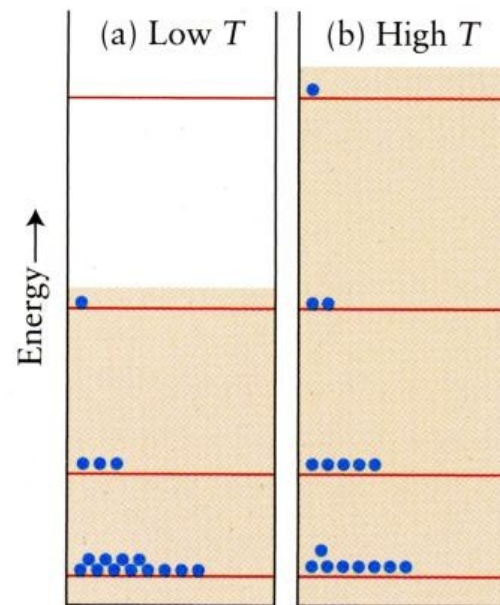


FIGURE 4G.5 More energy levels become accessible in a box of fixed width as the temperature is raised. The change from part (a) to part (b) is a model of the effect of heating an ideal gas at constant volume. The tinted band shows the range of thermally accessible levels. The average energy of the molecules also increases as the temperature is raised; that is, both internal energy and entropy increase with temperature.

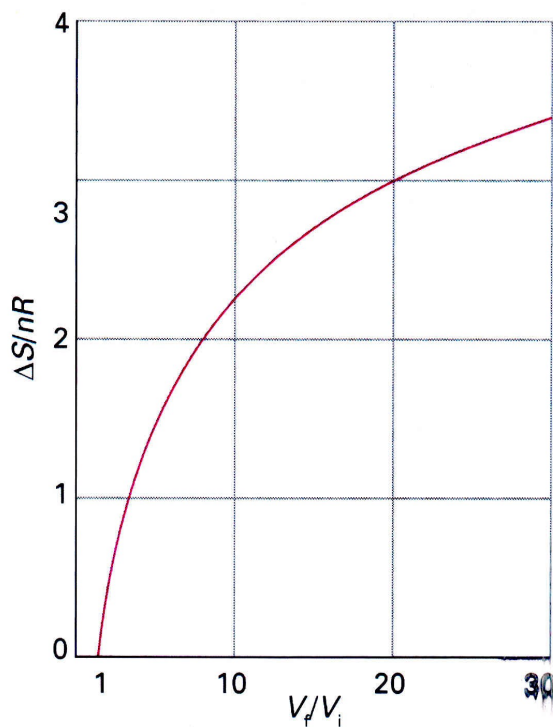


Fig. 3.12 The logarithmic increase in entropy of a perfect gas as it expands isothermally.

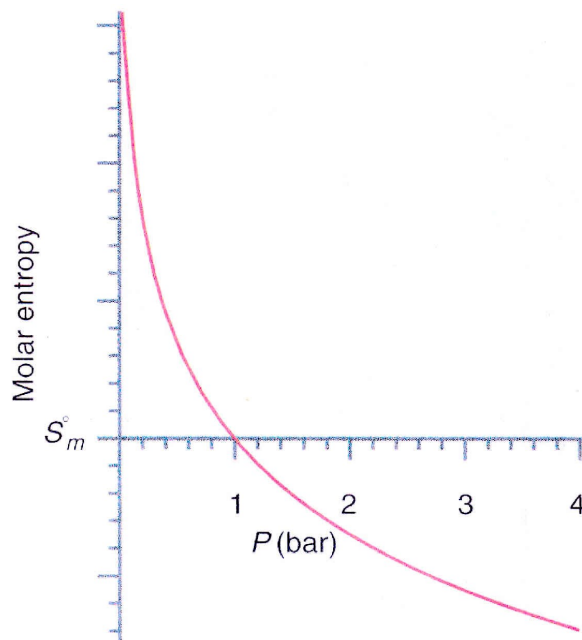


FIGURE 5.12

The molar entropy of an ideal gas is shown as a function of the gas pressure. By definition, at 1 bar, $S_m = S_m^\circ$, the standard state molar entropy.

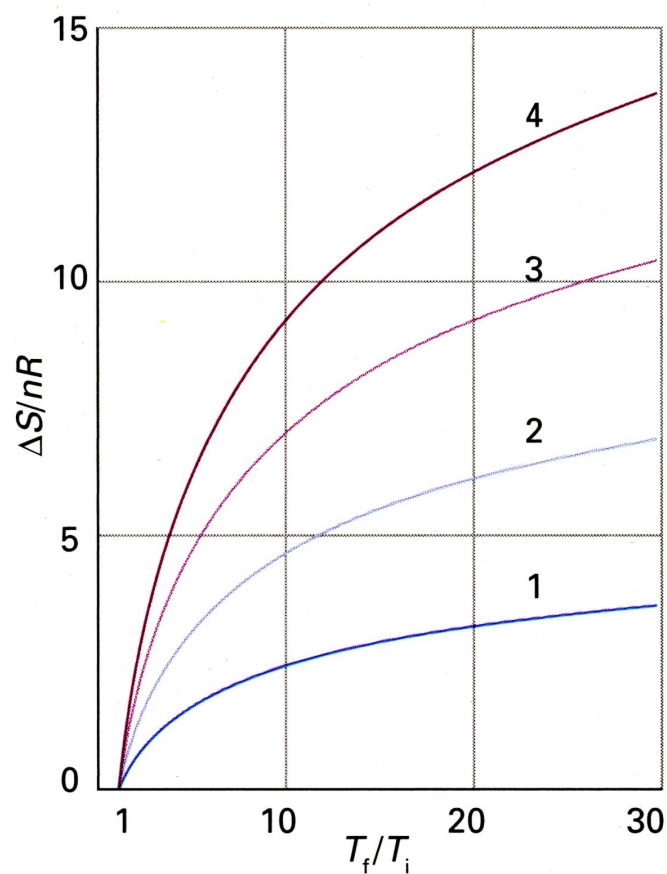
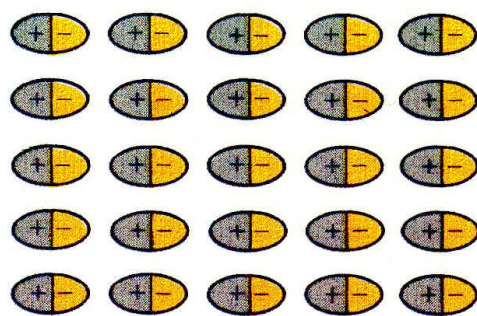
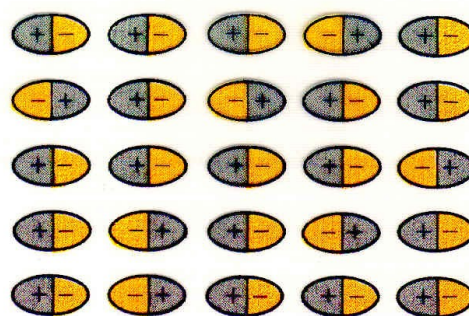


Fig. 3.13 The logarithmic increase in entropy of a substance as it is heated at constant volume. Different curves correspond to different values of the constant-volume heat capacity (which is assumed constant over the temperature range) expressed as $C_{V,m}/R$.

$$S = k_B \ln \Omega$$



(a)



(b)

$$\Omega = ?$$

$$S = ?$$

$$\Omega = ?$$

$$S = ?$$

Figure 10.11

(a) A perfect crystal of hydrogen chloride at 0 K; the dipolar HCl molecules are represented by



The entropy is zero ($S = 0$) for this perfect crystal at 0 K.

(b) As the temperature rises above 0 K, lattice vibrations allow some dipoles to change their orientations, producing some disorder and an increase in entropy ($S > 0$).

THIRD LAW OF THERMODYNAMICS