Figure 9-2: Molecular view of mixing: (a) pure component; (b) component in mixture; (c) component in mixture with the other components made invisible. In the mixed state a component has undergone isothermal "expansion" relative to the pure state. This gives rise to the entropy of mixing.

enthalpy of mixing ΔH_{mix}. Molecules in a mixture can assume more microscopic states compared to the pure components because they can be surrounded by various combinations of like and unlike species (see Figure 9-2). In molecular language, this means that the entropy of the mixture is higher than the entropy of the pure components combined, that is, $\Delta S_{\mathrm{mix}} > 0$. The enthalpy of mixing may be positive, negative, or zero. If it is negative (mixing is exothermic), it contributes to the decrease of ΔG_{mix} and acts as a further driving force for mixing. If it is positive (mixing is endothermic), it increases the value of ΔG_{mix} and opposes mixing. If it is zero it makes no contribution to the Gibbs free energy of mixing and the process is driven entirely by entropy. Exothermic mixing indicates favorable interaction between unlike components, which makes the separation of the mixture more difficult. Endothermic mixing indicates the opposite: interaction between unlike components is energetically unfavorable (energy must be supplied to form the mixture) and the mixture they form is easier to separate. The work required for the separation of the components is equal to the lost work of mixing because, as we recall, lost work refers to the work needed to reverse a process (in this case, to separate the components). From eq. (6.34), this work is

$$W_{\mathrm{lost}} = T_0 S_{\mathrm{gen}}.$$

The entropy generation consists of the entropy change of the system, ΔS_{mix}, and the entropy change of the surroundings, $-\Delta H_{\mathrm{mix}}/T$:[9]

$$S_{\mathrm{gen}} = \Delta S_{\mathrm{mix}} - \frac{\Delta H_{\mathrm{mix}}}{T}.$$

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9. For constant-pressure mixing, the amount of heat exchanged with the surroundings is $Q = \Delta H_{\mathrm{mix}}$; accordingly, the entropy change of the surroundings at temperature T is

$$-\frac{Q}{T} = -\frac{\Delta H_{\mathrm{mix}}}{T}.$$