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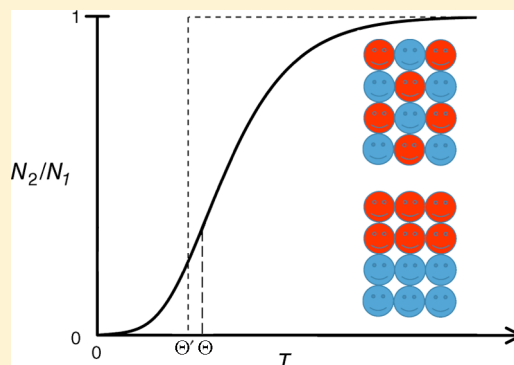
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# Entropy of Mixing of Distinguishable Particles

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**ABSTRACT:** The molar entropy of mixing yields values that depend only on the number of mixing components rather than on their chemical nature. To explain this phenomenon using the logic of chemistry, this article considers mixing of distinguishable particles, thus complementing the well-known approach developed for nondistinguishable particles, for example, ideal gases and solutions. The result is a simple quantitative treatment based on the Boltzmann distribution using the Gibbs paradox as a case study to define a macroscopic thermodynamic criterion of distinguishability. It is the presence of nonzero, albeit often small,  $\Delta H(\text{mixing})$  in a reversible process—due to a change in the energy of intermolecular interactions,  $\Delta \epsilon$ —that is responsible for the nonzero entropy. Temperature in the Clausius equation,  $dS_{\text{system}} = dq_{\text{rev}}/T$ , normalizes the heat—different in various processes—to yield the same entropy of mixing per mole, as long as this temperature,  $T = \Theta'(\text{mixing})$ , that of the reversible process, is linked to the Boltzmann characteristic temperature,  $\Theta = \Delta \epsilon/k = 2\Theta' \ln 2$ . For mixing exactly the same substances,  $dS_{\text{system}} = dq_{\text{rev}} = 0$ , and thus,  $\Theta'(\text{mixing})$  is undefined as a 0/0 uncertainty; the process can occur reversibly for any amount at any temperature. Two cases of negative entropy of mixing/expansion validate the suggested approach.



**KEYWORDS:** Graduate Education/Research, Upper-Division Undergraduate, Physical Chemistry, Misconceptions/Discrepant Events, Thermodynamics

The molar entropy of mixing depends only on the number of mixing components, not on their chemical nature. This fundamental feature of entropy is often difficult to grasp both by chemistry students and professionals because we ordinarily view particles as interacting with each other. The approach that was developed earlier for *indistinguishable* particles explains the occurrence of entropy of mixing by mutual expansion of independent species.<sup>1</sup> Although this approach is valid and useful, unifying various phenomena under one physical concept, it circumvents the problem stated above by assuming that the mixing gases and solutions are ideal.

To address the problem fundamentally via an explanation based on *chemistry*, this new study considers mixing of distinguishable, that is, *interacting* particles, in which there are low (near-zero) enthalpies of mixing. An even more urgent reason for considering the entropy of mixing of interacting particles is that several cases cannot be explained by using interaction-free models. (Cases 1 and 2 will be revisited after the entropy of mixing is considered in Case 3.)

- Case 1. In mixing amines with water, the molar  $\Delta S_{\text{system}}(\text{mixing})$  is *negative*.<sup>2</sup>
- Case 2. Real gas expansion may produce heat instead of absorbing it.<sup>3</sup> This means that when this process is conducted reversibly and isothermally, its entropy change is *negative*. Note that this heat reversal in gas expansion not only occurs under extremely high temperatures and pressures; for He and H<sub>2</sub>, such a negative entropy change occurs at ambient pressure with  $T < 200$  and  $T < 800$  K, respectively, so it cannot be ignored as something exotic.

- Case 3: The Gibbs paradox. Although the isothermal mixing of two very similar chemicals produces an entropy change of  $R \ln 2$  per mole, mixing of two identical chemicals does not. This paradox has created an extensive literature.<sup>4–9</sup> Its origin is in formulating thermodynamic distinguishability, but it can also be related to the coupling of two fundamental equations.

For Case 3: First, the Clausius equation relates the system entropy,  $dS_{\text{system}}$ , to the heat of a reversible process,  $dq_{\text{rev}}$ , and temperature

$$dS_{\text{system}} = dq_{\text{rev}}/T \quad (1)$$

Then, the Boltzmann-Planck equation, connecting the entropy of the system at a constant energy,  $S_{\text{system}}(E)$  and the number of equiprobable microstates,  $W$ , via the Boltzmann constant,  $k$

$$S_{\text{system}}(E) = k \ln W \quad (2)$$

emphasizes the *statistical* nature of entropy. Gibbs formulated his paradox as a *microscopic* phenomenon for very similar substances, isotopes being the outstanding case. If the particles are distinguishable, that is, distinctly different on a microscale, the entropy of mixing is calculated using eq 2. If the mixed substances are significantly different, the heat absorption upon mixing also becomes significant, yielding a clearly nonzero entropy value and coupling eqs 1–2. Thus, the Gibbs paradox becomes moot if one can demonstrate the inherent relation of

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the macroscopic (Clausius) and microscopic (Gibbs and Boltzmann) ways to calculate entropy.

The problem is that the heat value is hardly detectable, if at all, for mixing similar particles, that is, isotopes. Then, the inherent coupling of the two approaches is usually shown either quantitatively, using rather complex concepts of canonical ensembles, phase space, and quantum thermodynamics,<sup>4–9</sup> or qualitatively,<sup>9,10</sup> focusing on the microscopic aspects. For example, Spencer and Lowe pointed out in their pedagogically important study that the *R* and *S* isomers of a chiral substance have exactly the same masses and energy levels, despite different molecular structures spatially.<sup>10</sup> They explained the nonzero entropy of mixing by the particles' microscopic distinguishability at a high-temperature limit.

The aim of the current study is to find a relatively simple yet quantitatively correct conceptual connection between eqs 1–2, including the derivation of a new macroscopic criterion of thermodynamic distinguishability. The suggested approach is not applicable to inherently nondistinguishable/noninteracting particles, for example, an ideal gas or systems having ground state entropy,<sup>11</sup> for example, noninteracting spins.<sup>12</sup> I shall limit the scope of this study to what I call “fluids” henceforth, that is, liquid solutions, supercritical fluids, and relatively dense gases. Finally, only the mixing of equimolar amounts will be considered yielding molar thermodynamic values, to simplify the algebraic treatment by providing each particle with just two equiprobable options for interactions. One more apparent assumption, that both the  $\Delta H$  and  $\Delta S$  values are temperature-independent, will be eliminated toward the end of the discussion.

### “Experimental” Section

The stereotypical illustration of entropy of mixing involves a two-bulb apparatus in which the bulbs are connected by a stopcock that, when opened, allows mixing (complete mixing is assumed henceforth by default, unless otherwise stated). The disadvantage of such a system is that mixing conducted this way is irreversible, that is, may absorb less heat, if any. To enable reversible mixing, this apparatus should be modified by introducing hypothetical semipermeable membranes specific for each of the substances being mixed; the concomitant work needed to move the membranes compensates for the nonrecovered heat.

Table 1 lists several simple representative experiments pertinent to the Gibbs paradox that could be conducted using this hypothetical apparatus. Experiment 0 is a “blank”, whereas Experiment X is a “control” that involves expansion.

### Physical Nature of Molecular Distinguishability

One microscopic feature that unifies Experiments 0–4 is the energy difference created by transitory intermolecular interactions between the briefly existing nonequivalent pairs, for example, *RS* (*SR*) and *RR* (*SS*) diastereomer pairs. The nonzero heat of mixing results from *quasireactions*, in which weak intermolecular attractions, “bonds,” are constantly forming. As a result, the number of homointermolecular bonds is decreased because heterointermolecular bonds/attractions are present in equal quantities. The opposite process of separation releases heat; due to this energy difference, isotopes can be isolated upon cooling or by distillation,<sup>14–16</sup> whereas optical isomers can be separated using chiral chromatographic columns. Various “order-disorder” transitions, for example, those involving spin changes (“spin mixing”), result in the absorption

**Table 1. Virtual Experiments Conducted in a Two-Bulb System with a Different Substance in Each Connected by a Stopcock with Hypothetical Semi-Permeable Membranes Specific for Each of the Substances Being Mixed**

Experiment	Bulb 1	Bulb 2	$\Delta H(\text{mixing})$ magnitude	$\Delta S_{\text{rev}}$
X	Gas A	Vacuum	Not applicable <sup>a</sup>	$R \ln 2$
0	Fluid A	Fluid A	0	$\Delta S_{\text{mixing}}$ 0
1	Fluid A <sup>b</sup>	Fluid B <sup>b</sup>	Hardly detectable <sup>c</sup>	$R \ln 2$
2	Fluid A <sup>b</sup>	An isotope of A <sup>b</sup>	Hardly detectable	$R \ln 2$
3	Fluid A ( <i>R</i> ) <sup>d</sup>	Fluid A ( <i>S</i> ) <sup>d</sup>	Hardly detectable	$R \ln 2$
4	<i>para</i> -H <sub>2</sub>	<i>ortho</i> -H <sub>2</sub>	0 without a catalyst; substantial if at equilibrium <sup>13</sup>	$R \ln 2$

<sup>a</sup>Heat may be recovered if this process is conducted reversibly, that is, as an expansion against another gas followed by removal of the other gas using a specific semipermeable membrane. <sup>b</sup>Experiment X with one mole in Bulb 1. All others with one-half mole in each bulb. The conditions listed are those *before* the corresponding experiment. After each experiment, the contents of the entire system are homogeneous. Experiments 0–4 assume infinite time. <sup>c</sup>Liquid solutions should be near-ideal to qualify for the Gibbs paradox. <sup>d</sup>*R* and *S* stereoisomers of A, respectively.

of small amounts of heat when the system temperature increases above a certain threshold temperature.<sup>17–19</sup>

The resulting heat absorption upon mixing two substances at room temperature may be extremely small, yet it must occur to enable mixing as a reversible process. If  $\Delta S_{\text{rev}}(\text{mixing})$  is positive,  $\Delta H_{\text{rev}}(\text{mixing})$  must be positive as well to have  $\Delta G_{\text{rev}}(\text{mixing}) = \Delta H_{\text{rev}}(\text{mixing}) - T \Delta S_{\text{rev}}(\text{mixing}) = 0$ . This sign configuration will be assumed henceforth by default, although the opposite combination of negative  $\Delta H$  and negative  $\Delta S$ , for example, Cases 1 and 2, is also possible. For complete equimolar mixing

$$\Delta H(\text{mixing}) = -q_{\text{rev}}(\text{separation}) = \Delta \epsilon N_A / 2 \quad (3)$$

where  $N_A$  is Avogadro's number and  $\Delta \epsilon$  is the energy/enthalpy difference between the hetero- and homointermolecular interactions. Thus, both  $\Delta \epsilon$  and  $\Delta H(\text{mixing})$  are quantitative measures of the energy of intermolecular interactions, on the molecular and molar scales, respectively. Note that  $\Delta \epsilon$  does not necessarily pertain to particular intermolecular interactions, as in the case of mixing atoms. In complex molecules, multiple homo- and heterointermolecular interactions are possible, with different energy gaps. Yet, upon mixing, any specific homointermolecular interaction is replaced by its heterointermolecular counterpart. Thus, to separate the effect of mixing from system-specific effects, the following assumption is justified: when two different chemicals mix, all the different cases can be adequately represented by just one *effective* (average) energy gap,  $\Delta \epsilon$ , which can be calculated directly from macroscopic data,  $\Delta H$  (complete mixing), by using eq 3.

Although the energy of intermolecular interactions is proportional to the number of particles (eq 3), only half of the molecules exhibit heterointermolecular interactions in an equimolar homogeneous (complete) mixture. The half factor in eq 3 equals not only this fraction but also the mole fraction of each of the mixing components,  $x_i$ . Thereby, these mole fractions match the probabilities of homo- vs heteromolecular

interactions,  $p_1$  and  $p_2$ , respectively. This yields the molar Gibbs entropy, which in turn leads to the well-known formula for the entropy of mixing

$$\begin{aligned} \lim_{T \rightarrow \infty} \Delta S(\text{mixing}) &= \text{high-}T\text{-limiting } \Delta S \\ &= -kN_A \sum_{i=1}^n (p_i \ln p_i) = -kN_A \sum_{i=1}^n (x_i \ln x_i) \end{aligned} \quad (4)$$

The details of relationships between eqs 2 and 4 and the Gibbs entropy are provided elsewhere.<sup>20</sup> The use of the limiting value in eq 4 is explained in the next section.

How do *different* (numerically) energies of intermolecular interactions yield exactly the *same* limiting value for molar entropy of mixing? To address this question, the semi-permeable membranes in Experiments 1–4 of Table 1 should be removed. By default, at a randomly selected temperature (e.g., room temperature), mixing for near-ideal solutions then becomes irreversible—that is, complete—regardless of  $x_i$ . Also, the absorbed heat may not be recovered. However, Experiments 1–3 (and Experiment 4 in the presence of a catalyst) can still be performed reversibly at a specific temperature,  $T = \Theta'$ , yielding a zero free energy change in the  $\Delta G_{\text{rev}} = \Delta H_{\text{rev}} - \Theta' \Delta S_{\text{rev}}$  relation. So, for such reversible mixing under constant temperature and pressure, when heat is represented by  $\Delta H_{\text{rev}}$ , the Clausius equation becomes

$$\Delta S_{\text{rev}}(\text{mixing at } T = \Theta') = \Delta H_{\text{rev}}(\text{mixing at } T = \Theta')/\Theta' \quad (5)$$

Henceforth, entropy and enthalpy will be indexed as  $\Delta S_{\text{rev}}$  and  $\Delta H_{\text{rev}}$  only for reversible isothermal processes at  $T = \Theta'$ . Note that  $\Theta'$  is a *macroscopic* value. To address the Gibbs paradox, a similar *microscopic* value is introduced in the next section.

### Mixing from the Standpoint of the Boltzmann Distribution

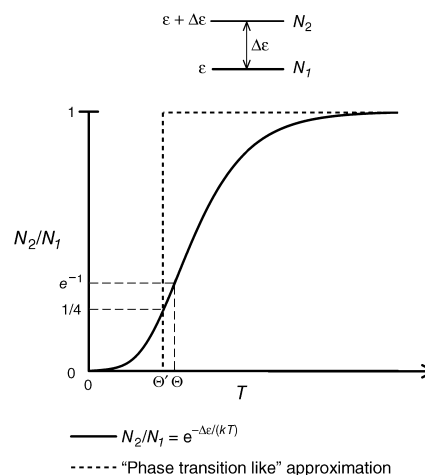
In my previous publications that considered intermolecular interactions, the Boltzmann distribution was applied to other related phenomena, for example, residual entropy<sup>20</sup> and molar entropy of neat liquids.<sup>21</sup> The noteworthy emphasis of the current study is that the  $\Theta'$  in eq 5 will be linked to  $\Theta = \Delta\epsilon/k$ , the Boltzmann characteristic temperature. This approach is fully applicable only as long as the solutions are near ideal, that is, the energy gaps are so small that promotion of particles to higher energy levels would not trigger other entropy changes.

Given this limitation and assuming thermal equilibrium, a system of two chemicals can be quantitatively described by the Boltzmann distribution of particles on two levels,  $\epsilon$  and  $\epsilon + \Delta\epsilon$ , where  $\Delta\epsilon$  is the energy difference between the low energy (homointermolecular interactions) and higher energy (heterointermolecular interactions) of the correspondingly aligned molecules (eq 6; the heterointermolecular interactions at the interface of immiscible phases will be neglected)

$$N_2/N_1 = e^{-\Delta\epsilon/kT} \quad (6)$$

where  $N_1$  and  $N_2$  are the populations of two pertinent energy levels reflecting the number of molecules exhibiting homo- and heterointermolecular interactions, respectively.

The significance of  $\Theta = \Delta\epsilon/k$  in mixing is illustrated in Figure 1. If two chemicals do not mix at all, the population of the second energy level is zero because all particles can interact only with those of their own kind;  $\Delta\epsilon \gg kT$ . Chemicals become soluble in each other when their temperature approaches  $\Theta$  ( $\Theta'$ ). When  $\Theta' \approx T$ , the microscopic counterpart



**Figure 1.** Ratio of heteromolecularly interacting ( $N_2$ ) and homomolecularly interacting ( $N_1$ ) molecules as functions of temperature.

of  $\Delta H(\text{mixing})$ , that is, the actual  $\Delta\epsilon$  between zero and the point on the sigmoidal curve at a given temperature, increases with temperature, as does the  $N_2/N_1$  ratio reflecting the fraction of mixed substances.

When  $T \gg \Theta$ , two chemicals are miscible with no limitations, so  $N_1 = N_2$ ; there are as many heterointermolecular contacts as homointermolecular. The effective dimensionless energy gap,  $\Delta\epsilon/kT$ , becomes near zero;  $N_2 = N_A/2$  particles absorb the corresponding amount of energy,  $\Delta\epsilon N_A/2$  matching  $\Delta H(\text{mixing})$  in eq 3. The resulting  $\Delta S(\text{mixing}) = k \ln (W_2/W_1) = k \ln [N!/(N_2!N_1!)] = R \ln [N_A!/(N_A/2)!^2] = R \ln 2$  using the Stirling approximation.<sup>20,21</sup> For near-ideal solutions characterized by low  $\Delta\epsilon$ , room temperature may be considered infinitely high ( $T \gg \Delta\epsilon/k$ ). This is a justification of the practical use of eq 4 at ambient temperature. The link between the macroscopic  $\Theta'$  and microscopic  $\Theta$  to address the Gibbs paradox is provided next.

### Connection between the Clausius Equation and the Boltzmann Distribution

Because of the steep rise of exponential functions, a simplified view of this process is that the components of a mixture would either mix or separate reversibly at  $\Theta' + dT$  and  $\Theta' - dT$ , respectively, that is, treating mixing as an isothermal phase transition

$$\begin{aligned} \lim_{T \rightarrow \infty} \Delta S(\text{mixing}) &= \text{high-}T\text{-limiting } \Delta S(\text{mixing}) \\ &= \text{fully recovered } \Delta H(\text{mixing})/\Theta' \end{aligned} \quad (7)$$

To fully recover the  $\Delta H(\text{mixing})$  shown in eq 7, the process should be conducted reversibly over the entire temperature range using the path shown as a sigmoidal curve in Figure 1, rather than isothermally. If the starting temperature of this process is not significantly lower (or even higher) than  $\Theta'$ , only a fraction of this heat can be recovered. This explains why the heat of mixing similar substances conducted at room temperature often cannot be detected. The fully recovered  $\Delta H(\text{mixing})$ , by the way it is defined in eq 7, equals  $\Delta H(\text{mixing})$  in eq 3. The other advantage of using eq 7 is that it contains the high- $T$ -limiting  $\Delta S(\text{mixing}) = R \ln 2$ . I shall show that a simple link exists between eqs 5 and 7.

Because  $\Theta = \Delta\epsilon/k = 2\Delta H(\text{mixing})/R$  (eq 3), whereas  $\Theta' = \Delta H(\text{mixing})/(\text{high-}T\text{-limiting } \Delta S) = \Delta H(\text{mixing})/R \ln 2$  (eq



7),  $\Theta = 2\Theta' \ln 2$ . This is the algebraic link between the macroscopic  $\Theta'$  and microscopic  $\Theta$ . Using eq 6 for  $T = \Theta'$ ,  $N_2/N_1 = \exp(-\Theta/\Theta') = \exp(-2 \ln 2) = \exp(\ln(1/4)) = (1/4)$ .  $\ln(1/4)$  can be presented as  $\ln[1/2 \times 1/2]$ , that is, half of the chemicals present mix (this fraction is temperature-dependent), with half of this half of molecules statistically exhibiting heterointermolecular interactions (as inherent for any equimolar homogeneous mixture). The first of these half factors connects the  $\Delta H(\text{mixing})$  and  $\Delta H_{\text{rev}}(\text{mixing})$  in eqs 7 and 5, respectively, whereas the second connects  $\Delta \varepsilon$  and  $\Delta H(\text{mixing})$  in eq 3.

As for the entropy, upon the exclusion of the nonmixed phase containing  $N_A/2$  particles,  $N_2/N_1 = (1/4)$  can be used in eq 4 as  $x_i$  yielding  $\Delta S_{\text{rev}}(\text{mixing}) = -(1/2)kN_A((1/4) \ln(1/4) + (1/4) \ln(1/4)) = -R((1/4) \ln(1/4)) = (1/2)R \ln 2$ . Alternatively, using the equipartitioning of  $N_A/2$  particles among two energy levels,  $\Delta S_{\text{rev}}(\text{mixing}) = (1/2)kN_A \ln W_2/W_1 = (1/2)kN_A \ln [(N_A/2)!/(N_A/4)!^2] = (1/2)R \ln 2$  by applying the Stirling approximation. Thus, at  $T = \Theta'$ , both  $\Delta H_{\text{rev}}$  and  $\Delta S_{\text{rev}}(\text{mixing})$  are half of their limiting values.

Now, the key question may be addressed, why entropy of mixing is the same for different substances. For near-ideal solutions, for example, isotopes,  $\Theta' = \Delta \varepsilon/2k \ln 2$  corresponds to a very low  $\Delta H_{\text{rev}}(\text{mixing})$  according to eq 3. However, the combination of eqs 3, 5 and 7 effectively removes  $\Delta \varepsilon$  from further consideration;  $\Delta S(\text{mixing})$  is not a function of the value of the energy involved. When using eq 1, both  $\Delta H_{\text{rev}}(\text{mixing})$  and  $\Delta H(\text{mixing})$  are normalized by  $\Theta'$ .

### Macroscopic Criterion for Thermodynamic Distinguishability: What Students Should Know

A finite value of  $\Theta'$  implies that at  $T \approx \Theta'$  the extent of mixing depends on the molar ratio of substances mixed; unlimited miscibility is observed only at  $T \gg \Theta'$ . The occurrence of a defined  $\Theta'$  offers a new macroscopic criterion for thermodynamic distinguishability; it is tantamount to a nonzero  $\Delta H(\text{mixing})$ . Distinguishability in a mixture shows up as a significant decline of mutual solubility at  $T \approx \Theta'$ , with a near-complete phase separation at  $T \ll \Theta'$ .<sup>22</sup>

By contrast, for truly ideal solutions, that is, for mixing the same substances,  $\Delta H(\text{mixing}) = 0$ .<sup>23</sup> The fact that this leads to  $\Delta S(\text{mixing}) = 0$  implies that  $\Theta'$  is not defined as a 0/0 uncertainty (eqs 5 and 7), that is, reversible mixing occurs for any amounts at any temperature, with no heat effects. This section may be used as a summary of what students should know about distinguishability.

### Returning to Two Cases Featuring Negative Entropy of Mixing/Expansion

#### Case 1, Negative $\Delta S(\text{mixing})$ of Amines with Water.

This phenomenon is due to negative  $\Delta H(\text{mixing})$  and  $\Delta \varepsilon$  between homo- and heterointermolecular interactions because in these cases the heterointermolecular hydrogen bonding is stronger than its homointermolecular counterpart.<sup>2</sup> Within a suitable (narrow) temperature range, mixing equimolar amounts of two such components results in the formation of a regularly structured solution when each nitrogen of an amine forms a hydrogen bond with water. However, outside the temperature range where hydrogen bonding is applicable, mixing becomes endothermic even for such chemicals.

**Case 2, Heat Release upon Helium and Hydrogen Gas Expansion.**<sup>3</sup> For these two gases within a near-ambient  $P$ – $T$  range, intermolecular interactions become stronger upon expansion, in contrast to other gases. Goussard and Roulet

suggested that the general repulsive nature of helium and hydrogen, when atoms significantly encroach on one another at relatively large interparticle distances, need be considered in combination with significant kinetic energy, which brings the gas molecules close enough to each other.<sup>3</sup> This makes the mean effective intermolecular interaction repulsive, even if the average intermolecular distance exceeds the sum of Van der Waals radii.<sup>3</sup> If  $\Delta H_{\text{rev}}(\text{expansion})$  is negative,  $\Delta S_{\text{rev}}(\text{expansion})$  must also be negative to have  $\Delta G_{\text{rev}}(\text{expansion}) = 0$ .

## CONCLUSION

The presence of nonzero, albeit often small,  $\Delta H(\text{mixing})$  in a reversible process of intermolecular bond formation leads to a nonzero entropy for interacting particles. The balance of  $\Delta H_{\text{rev}}(\text{mixing})$  and the characteristic temperature for mixing two substances in equimolar amounts yields the molar  $\Delta S(\text{mixing})$ , which equals  $R \ln 2$  at  $T \gg \Theta$ , the Boltzmann characteristic temperature of mixing. Isothermal mixing of different substances occurs reversibly only at  $T = \Theta' = \Theta/2 \ln 2$ . For mixing the same substances, both  $\Delta H(\text{mixing})$  and  $\Delta S(\text{mixing})$  equal zero. Then,  $\Theta'$  is not defined, that is, reversible mixing occurs at any temperature for any amounts.

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### Notes

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- (22) One practical limitation in using this criterion is that the extremely low  $\Theta'$  for near-ideal solutions may not be attainable below the freezing point if it is larger than  $\Theta'$ , as in the case of isotopes in Experiment 2. This experiment then yields residual entropy.<sup>20</sup>
- (23) The process must be truly reversible to recover heat, as emphasized by Experiment 4. When *ortho*- and *para*-H<sub>2</sub> are mixed at any temperature, including  $\Theta'$ , no heat is absorbed because the system is not at equilibrium. But once a catalyst is added to speed up the achievement of equilibrium, a significant amount of heat is absorbed.<sup>13</sup>
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