Gibbs Paradox of Entropy of Mixing

Facts and Results

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Gibbs paradox: Entropy of mixing *decreases discontinuously* with similarity.

$$(\Delta S)_{\text{distinguishable}} = 2R \ln 2 = 11.53 \text{ JK}^{-1}$$

$$(\Delta S)_{\text{indistinguishable}} = 0$$

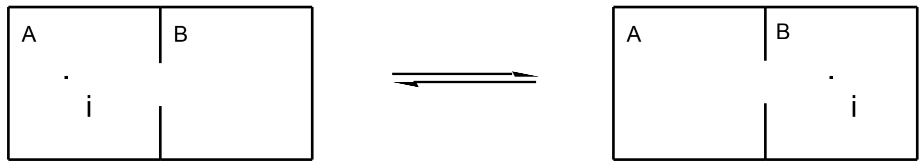
$$Q = \frac{1}{N!} q^N$$

- applicable to the formation of solid , liquid, gaseous mixtures.
- Foundation of statistical mechanics and quantum theory
- The resolutions of this paradox has been very *controversial* for over one hundred years.

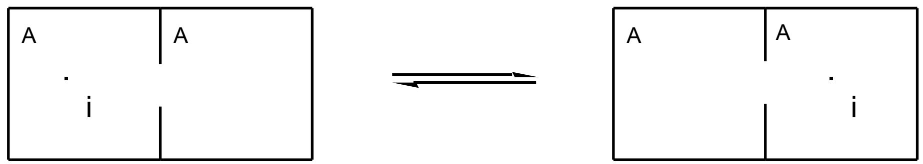
J. von Neumann, *Mathematical Foundations of Quantum Mechanics*, (Princeton University Press, Princeton, 1955), chap.5

Fact 1. Particle Diffusion

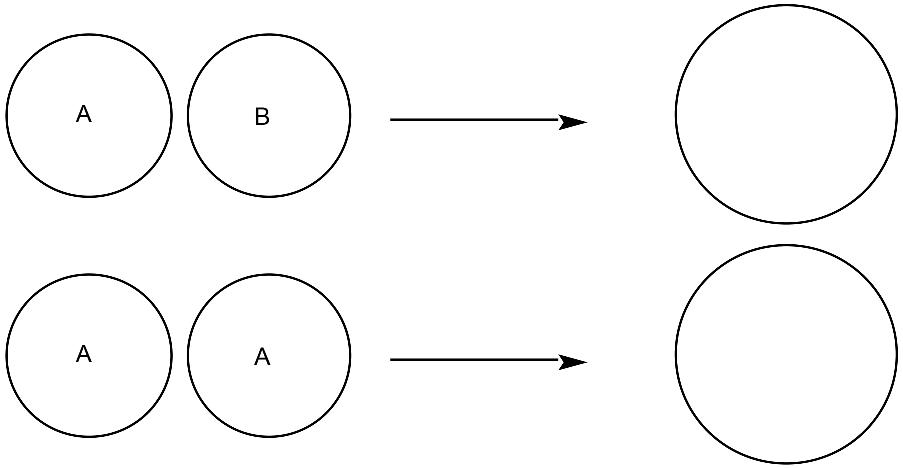
(a)



(b)



Fact 2. Mixing of Hydrocarbons in Water



Process	T (K)	TΔS	ΔH	ΔG
n-C_4H_{10} in water to liquid *n*-butane	298	6.85	1.00	-5.85
benzene in water to liquid benzene	291	4.07	0.00	-4.07

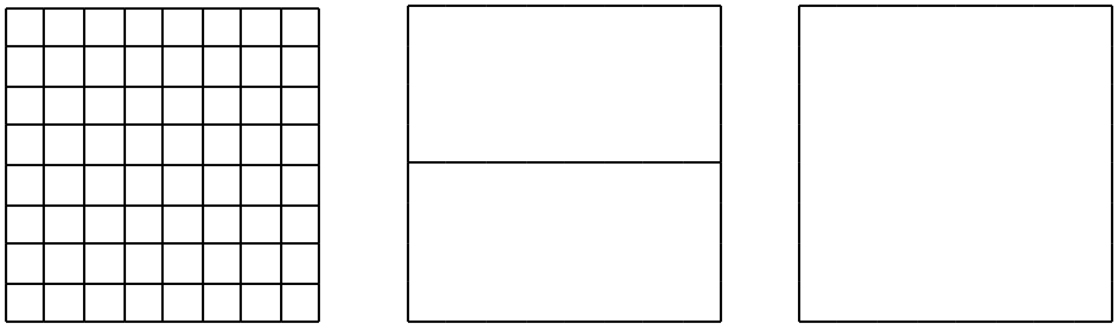
Fact 3. Entropy of a Crystal *vs*. Entropy of a Gas

the entropy of an ideal crystal is greater than that of the corresponding ideal gas by including a factor $1/N!$ in the partition function expression for gas

$$S_{\text{crystal}} - S_{\text{gas}} = k_{\mathrm{B}} \ln \left(\frac{w_{\text{crystal}}}{w_{\text{gas}}} \right)$$

$$= k_{\mathrm{B}} \ln N!$$

$$= k_{\mathrm{B}} N(\ln N - 1)$$



N subsystems | 2 subsystems | 1 system

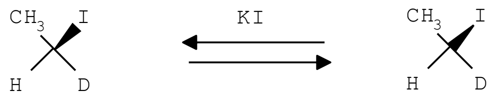
More constraints are removed →

Entropy increasing direction →

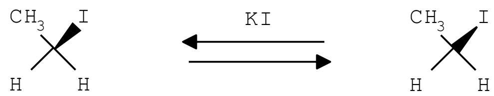
Fact 4. No-Reaction Reactions

Indistinguishable energy levels**:**

(a)



(b)



Distinguishable energy levels**:**

$$A \longrightarrow B$$

Fact 5. High-Throughput Screenings and molecular diversity

Preparation of two mixtures:

Different Molecules

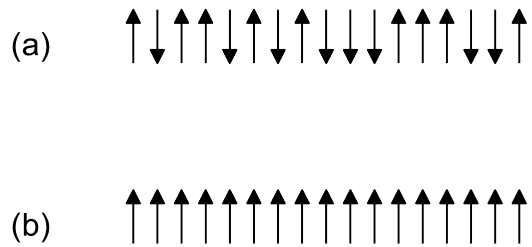
Very Similar or

Indistinguishable

Molecules

Fact 6. Second-Order Phase Transitions

Two static structures:



Fact 7. Mixing of Quantum States and Valence Bond Structures

$$\psi = c_1 \psi_1 + c_2 \psi_2 + \cdots$$

(a) $H^{\cdot}\ {}^{+}H$ $\qquad$ $H^{+}\ {}^{\cdot}H$

(b)

Rejection of Gibbs Paradox Statement

$$S_{\max} = \ln w \qquad\qquad S = -\sum_{k=1}^{w} p_k \ln p_k = \ln w_a$$

w —symmetry number; w_a —apparent symmetry number

$$-\sum_{k=1}^{w} p_k \ln p_k \leq \ln w$$

$$\text{Similarity: } Z = \frac{S}{S_{\max}} = -\frac{\sum_{i=1}^{w} p_i \ln p_i}{\ln w}$$

Entropy of mixing *increases continuously*.

Disproof of Gibbs Paradox Statement

Symmetry

Gibbs paradox statement implies that entropy decreases with the increase in symmetry (as represented by a symmetry number σ; see any statistical mechanics textbook).

Higer symmetry, lower entropy: $S = -\ln w$ e.g. $S = -\ln N!$

From group theory any system has at least a symmetry number *w*=1 which is the identity operation for a strictly asymmetric system. It follows that the entropy of a system is equal to, or *less* than, zero:

$$S \leq 0$$

Entropy is defined as non-negative.

- Therefore, this statement is false.

Because so far the Gibbs paradox statement has been factually a very fundamental assumption in conventional thermodynamics and statistical mechanics, it should not be a surprise if the rejection of this statement result in tremendous, very significant and very useful theoretical consequences in

Theoretical Physics
Physical Chemistry
Biophysics