Lecture-6

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What is Entropy?

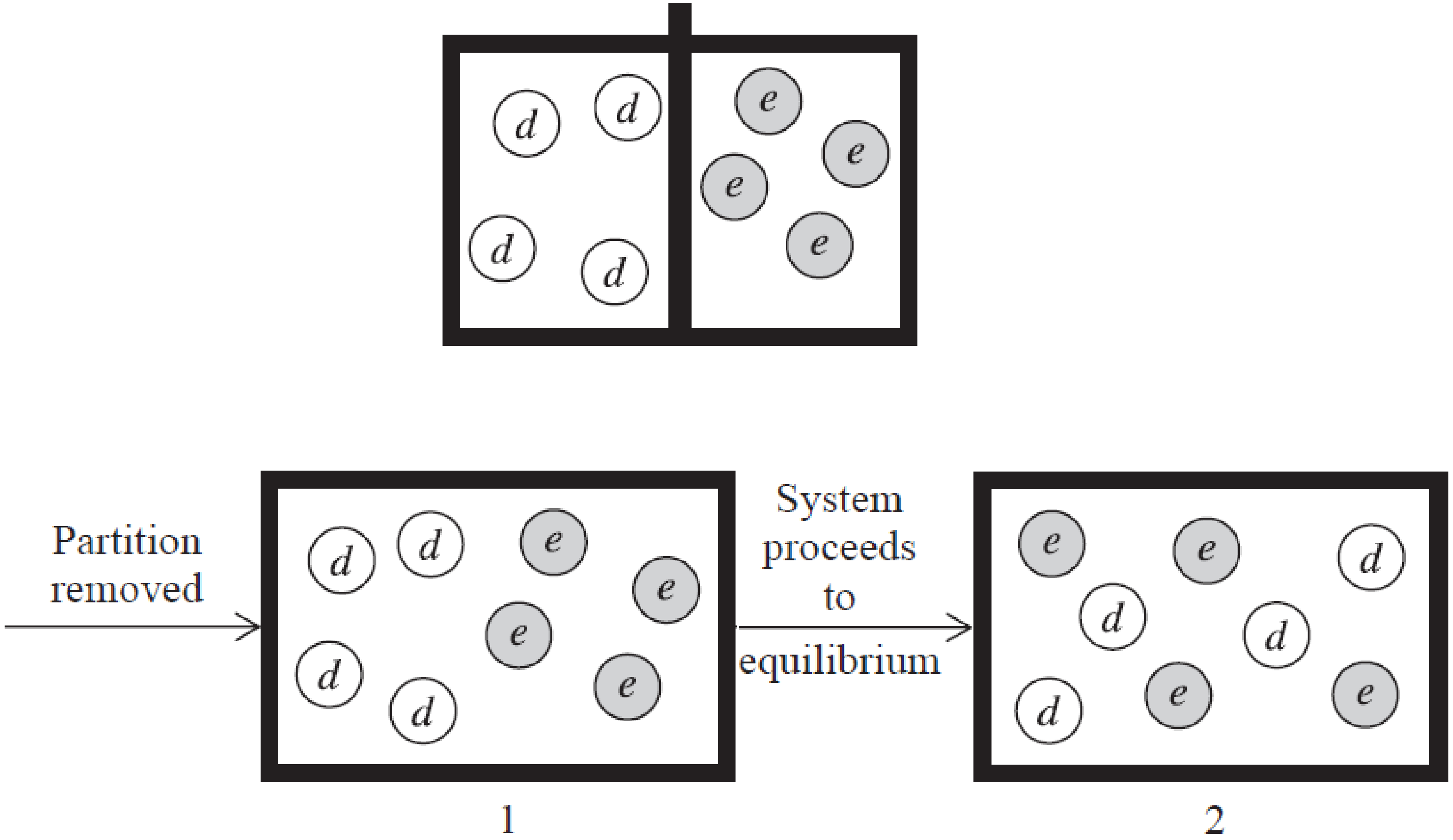
Each of the first three laws of thermodynamics leads to the existence of a state function.

- The zeroth law leads to temperature.
- The first law leads to internal energy.
- The second law leads to entropy.

Thermodynamics only tell us how to measure T, ΔU, and ΔS.

- Temperature is readily interpreted as some sort of measure of the average molecular energy.
- Internal energy is interpreted as the total molecular energy.
- Entropy is a measure of randomness or chaos. An increase of entropy means an increase of randomness of the system.

Molecular Interpretation of Entropy

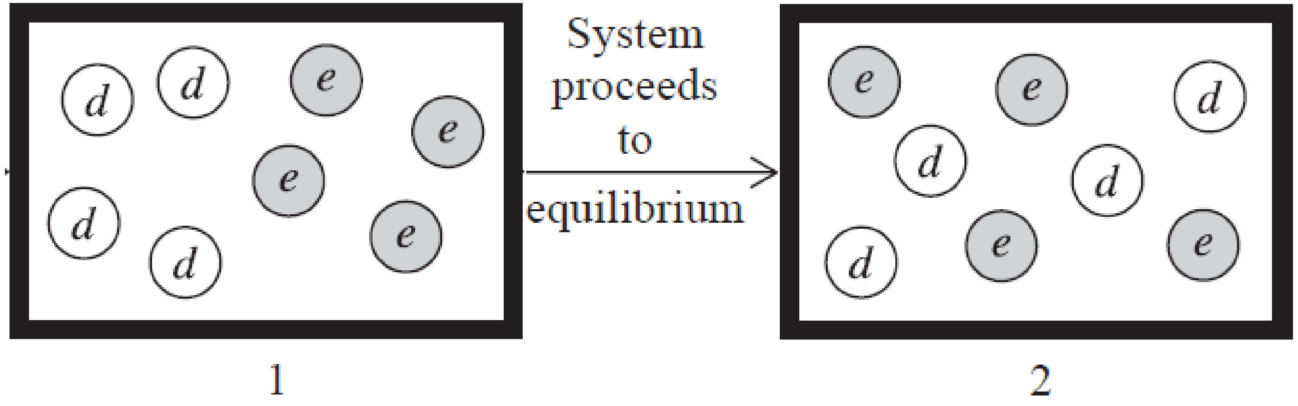


Nonequilibrium state

Equilibrium state

Irreversible mixing of perfect gases at constant *T* and *P*.

Why is the passage from the unmixed state 1 to the mixed state 2 irreversible?

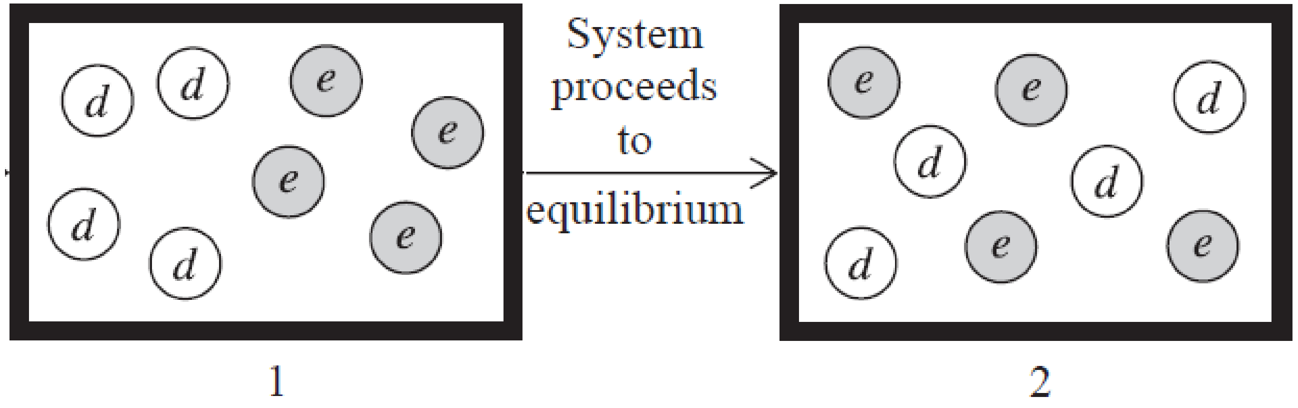


Nonequilibrium state

Equilibrium state

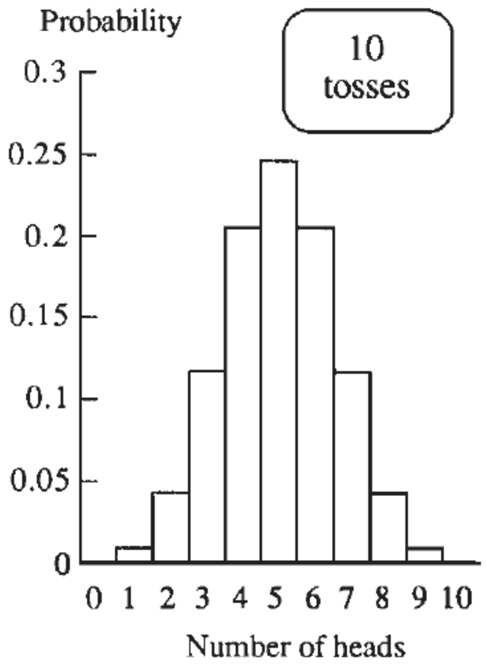
Clearly the answer is *probability.*

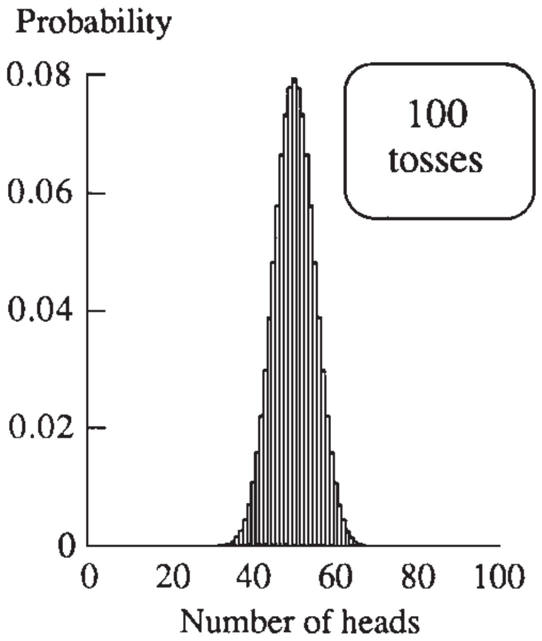
- If the molecules move at random, any *d* molecule has a 50% chance of being in the left half of the container.
- The probability that all the *d* molecules will be in the left half and all the *e* molecules in the right half (state 1) is extremely small.
- The most probable distribution has *d* and *e* molecules each equally distributed between the two halves of the container (state 2).



Nonequilibrium state

Equilibrium state





The probabilities for obtaining various numbers of heads for 10 tosses of a coin.

The probabilities for obtaining various numbers of heads for 100 tosses of a coin.

As the number of tosses increases, the probability of significant deviations from 50% heads diminishes

- An analogy to the spatial distribution of 1 mole of *d* molecules would be tossing a coin 6×10^{23} times.
- The chance of getting 6×10^{23} heads is extremely tiny.
- The most probable outcome is 3×10^{23} heads and 3×10^{23} tails, and only outcomes with a very nearly equal ratio of heads to tails have significant probabilities.
- The probability maximum is extremely sharply peaked at 50% heads.

Entropy and Probability

- The equilibrium thermodynamic state of an isolated system is the most probable state.
- The increase in *S* as an isolated system proceeds toward equilibrium is directly related to the system's going from a state of low probability to one of high probability.
- Therefore, the entropy *S* of a system is a function of the thermodynamic probability (*W)* of the system in a given state:

$$S = f(W) = k \ln W$$

where,
k is the Boltzmann constant and

Examples of entropy increasing situations

- Increase of temperature
- Increase of volume
- Solid state → Liquid state → Gaseous state
- Reactant → More than one products
- A reaction in which the number of moles of gas increases