

Focus 3: The Second and Third Laws

Entropy

Entropy changes of processes

Entropy measurement

Gibbs free energy

Combining 1st and 2nd law

The second law

The entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{\text{tot}} > 0$

Entropy (a state function) – A measure of the distribution of energy and matter.

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System of
interest

Thermodynamic definition of S

$$dS = \frac{dq_{\text{rev}}}{T}$$

Infinitesimal change in the system's entropy during a small reversible transfer of heat at temperature T

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$$q = -w$$

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$$\Delta S = nR \ln \frac{V_f}{V_i}$$

$$\Delta S_m = R \ln \frac{V_f}{V_i}$$

$$\Delta S_{\text{surr}}$$

$$dS = \frac{dq_{\text{rev}}}{T}$$

For System

$$\Delta S_{\text{surr}}$$

$$dS = \frac{dq_{\text{rev}}}{T}$$

For System

$$dq_{\text{sur}} = dU_{\text{sur}}$$



$$dS_{\text{sur}} = \frac{dq_{\text{sur}}}{T_{\text{sur}}}$$

For Surrounding

- In large reservoirs, we often simplify $dq_{\text{sur}} = dq_{\text{sur}} + dw_{\text{sur}}$ to $dq_{\text{sur}} = dq_{\text{sur}}$ by focusing on heat, because the work has a negligible effect on the reservoir's state.

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calculate the entropy change in the surroundings when 1.00 mol $\text{H}_2\text{O}(\text{l})$ is formed from its elements under standard conditions at 298 K, use $\Delta_{\text{f}}H^{\ominus} = -286 \text{ kJ mol}^{-1}$

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$$\Delta S_{\text{sur}} = \frac{2.86 \times 10^5 \text{ J}}{298 \text{ K}} = +960 \text{ J K}^{-1}$$

Statistical definition of entropy

$$S = k \ln \mathcal{W}$$

Boltzmann formula for the entropy

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number of **microstates**

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Mid Term 1 - Practice Question

A chemical reaction takes place in a container with cross-sectional area **75.0 cm²**. As a result of the reaction, a piston is pushed out through **25.0 cm** against an external pressure of **150 kPa**. **Calculate the work** done by the system.

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cross-sectional area times the linear displacement

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$$w = -(150 \times 10^3 \text{ Pa}) \times (1.87 \times 10^{-3} \text{ m}^3) \qquad 1 \text{ Pa} \cdot \text{m}^3 = 1 \text{ J}$$

$$w = -281 \text{ J}$$