Statistical Molecular Thermodynamics

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Video 6.9

Review of Week 6

Critical Concepts from Week 6

- Entropy is a state function defined by $dS = \frac{\delta q_{rev}}{T}$

- For an isolated system at constant U and constant V, spontaneous processes occur until entropy is maximized, after which point the system will be at equilibrium and only reversible processes will occur.

- The Second Law states that $dS \geq \frac{\delta q}{T}$ or $\Delta S \geq \int \frac{\delta q}{T}$ where the inequality holds for a process that is at any stage irreversible.

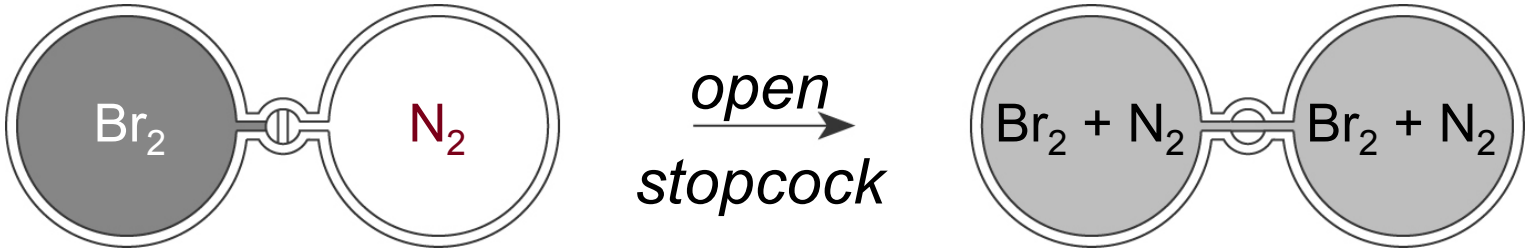
- Clausius' summary of the First and Second Laws states: The energy of the Universe is constant; the entropy is tending to a maximum.

Critical Concepts from Week 6

- The Boltzmann statistical mechanical definition of entropy, i.e., $S = k_B \ln W$ is maximized when the total number of systems in a microcanonical ensemble are distributed equally among all degenerate energy states
- An alternative definition of statistical entropy is $S = k_B \ln \Omega$ where Ω is the degeneracy of the system (or ensemble)
- The molar entropy change for the isothermal expansion of an ideal gas, from V_1 to V_2, is $R \ln(V_2/V_1)$; this is true whether the expansion is done reversibly or irreversibly, but the *sum* of the entropy changes of the gas and of the surroundings will be greater than zero if the expansion is irreversible at any point

Critical Concepts from Week 6

- The entropy of mixing for multiple volumes of equivalent substances is



$$\Delta S_{\text{mix}} = -R\sum_i n_i \ln y_i$$

where, $y_i = \dfrac{n_i}{\sum_j n_j}$ *mole fraction*

always greater than zero, so mixing is spontaneous

- The probability form of the entropy, $S = -k_{\text{B}}\sum_j p_j \ln p_j$ is maximized when all probabilities are equal and permits direct connection to the partition function

Critical Concepts from Week 6

- Using the partition function, $S = k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B \ln Q$

- The dependence of entropy on temperature and volume is

$$d\overline{S} = \overline{C}_v \frac{dT}{T} + R \frac{dV}{\overline{V}}$$

- The maximum efficiency of a (Carnot) engine is $1 - T_c/T_h$ where the engine does work using heat extracted from a hot reservoir at T_h and delivers unused heat to a cold reservoir at T_c
- Lord Kelvin's restatement of the Second Law is that no net work can be obtained from an isothermal process
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