

PHYSICAL CHEMISTRY

Chapter 5: The Second Law of Thermodynamics

5.1. Spontaneous Processes

- The reverse of a spontaneous process won't happen under the same conditions
- Viewing events with the random movement of many molecules makes certain events very unlikely to occur (i.e., these events would require the synchronization of a huge number of molecules)
- Cannot base spontaneity on a system losing energy (although this is common for spontaneous events), but rather entropy

Significant examples:

- Ball bouncing and losing thermal energy with each bounce; reverse process (gaining thermal energy from ground and rising up) cannot be spontaneous (intuitively)

5.2. Entropy

- Statistical definition of entropy: entropy is proportional to the number of molecules N , and probability is related to an exponential function of N , so let entropy $S \propto \ln W$, S is entropy, W is probability
 - Let the proportionality constant be k_B (Boltzmann's constant), so $S = k_B \ln W$
 - Because S is a state function, the path doesn't matter
 - For calculating changes in entropy: $\Delta S = S_2 - S_1 = k_B \ln \frac{W_2}{W_1}$
 - For a gas, $W = (CV_1)^N$ (approximately volume raised to the N th number of molecules), so
$$\Delta S = k_B \ln \left(\frac{V_2}{V_1} \right)^N = nR \ln \frac{V_2}{V_1}$$
 - Only for isothermal expansion, because entropy is affected by temperature
- Thermodynamic definition of entropy: $\Delta S = \frac{q_{rev}}{T}$ (or $dS = \frac{dq_{rev}}{T}$)
 - Derivation: For an isothermal, reversible expansion:
$$q = -w; q_{rev} = nRT \ln \frac{V_2}{V_1} \Rightarrow \frac{q_{rev}}{T} = nR \ln \frac{V_2}{V_1} = \Delta S$$
 - Note that this equation works for all substances (not only gases)
 - Note that this equation requires the reversible q (even though $\Delta S_{rev} = \Delta S_{irrev}$ because state function, this calculation requires q_{rev})

Significant examples:

- Likelihood of finding N molecules in half a container vs. the whole container

5.3. The Carnot Heat Engine

- A heat engine converts heat to mechanical work (e.g., steam engines and steam-powered electricity generators)
- Carnot heat engine is an idealized heat engine of one mole of gas with four steps:
 - Four steps:
 - Isothermal, reversible expansion from V_1 to V_2 (at T_2)
 - Adiabatic, reversible expansion from V_2 to V_3 ($T_2 \rightarrow T_1$)
 - Isothermal, reversible compression from V_3 to V_4 (at T_1)
 - Adiabatic, reversible compression from V_4 to V_1 ($T_1 \rightarrow T_2$)
 - Properties:
 - $\Delta U(\text{cycle}) = 0$

- $q(\text{cycle}) = RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3}$
 - $q_2 = RT_2 \ln \frac{V_2}{V_1}$ (heat absorbed from heat reservoir, positive value)
 - $q_1 = RT_1 \ln \frac{V_4}{V_3} = -RT_1 \ln \frac{V_2}{V_1}$ (heat discharged to cold reservoir, negative value)
- $w(\text{cycle}) = -RT_2 \ln \frac{V_2}{V_1} + \bar{C}_V(T_1 - T_2) - RT_1 \ln \frac{V_4}{V_3} + \bar{C}_V(T_2 - T_1) = -RT_2 \ln \frac{V_2}{V_1} - RT_1 \ln \frac{V_4}{V_3}$
 - From volume equation below, $w(\text{cycle}) = -R(T_2 - T_1) \ln \frac{V_2}{V_1}$
- $\frac{V_2}{V_1} = \frac{V_3}{V_4}$
 - Derivation: $P_1 V_1 = P_2 V_2; P_3 V_3 = P_4 V_4; P_2 V_2^\gamma = P_3 V_3^\gamma; P_1 V_1^\gamma = P_4 V_4^\gamma;$
 $\frac{P_2 V_2^\gamma}{P_1 V_1^\gamma} = \frac{P_3 V_3^\gamma}{P_4 V_4^\gamma} \Rightarrow \frac{P_2 V_2}{P_1 V_1} \times \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \frac{P_3 V_3}{P_4 V_4} \times \left(\frac{V_3}{V_4}\right)^{\gamma-1} \Rightarrow \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1}$
- Thermodynamic efficiency is the ratio of work done by heat engine to heat absorbed by engine (efficiency = $\frac{\text{net work done by heat engine}}{\text{heat absorbed by engine}} = \frac{|w|}{q}$)
 - For Carnot engine, efficiency = $\frac{R(T_2 - T_1) \ln \frac{V_2}{V_1}}{RT_2 \ln \frac{V_2}{V_1}} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$
 - Cannot be totally efficient; efficiency maximized by maximizing difference between T_1 and T_2
- For any cyclic process, $\sum_i \frac{q_i}{T_i} = \sum_i \Delta S_i = 0$
- Refrigerators, air conditioners, and heat pumps reverse the flow of spontaneous heat flow by applying work: $-q_2 = q_1 + w$
 - Coefficient of performance (COP) is measure of refrigerator or air conditioner's performance: $\text{COP} = \frac{q_1}{w} = \frac{T_1}{T_2 - T_1}$; gives the maximum COP value because it uses reversible heat value
 - COP for heat pumps is $\frac{T_2}{T_2 - T_1}$; more efficient than an electric heater

5.4. The Second Law of Thermodynamics

- Total change in entropy for a reversible process, $\Delta S_{\text{surr}} = 0$, $q_{\text{surr}} = -q_{\text{sys}}$
 - For an irreversible process, $\Delta S_{\text{univ}} \geq 0$

5.5. Entropy Changes

- Entropy change for reversible, isothermal expansion of an ideal gas is $nR \ln \frac{V_2}{V_1}$
- $\Delta_{\text{mix}} S = n_A R \ln \frac{V_A + V_B}{V_A} + n_B R \ln \frac{V_A + V_B}{V_B}$ for mixing of two gases (can be thought of as two gas expansions)
 - $\Delta_{\text{mix}} S = -R(n_A \ln x_A + n_B \ln x_B)$ (greater than 0, so spontaneous)
- $\Delta_{\text{fus}} S = \frac{\Delta_{\text{fus}} H}{T_f}$ (because enthalpy of fusion is equal to reversible heat)
 - Trouton's rule is an empirical observation that many liquids have a similar entropy of vaporization (because of similar structures of most liquids and gases)

- $\Delta S = C_p \ln \frac{T_2}{T_1}$ when heating