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
  \[ dS = \frac{\delta q_{\text{rev}}}{T} \]

- 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
  \[ dS \geq \frac{\delta q}{T} \quad \text{or} \quad \Delta S \geq \int \frac{\delta q}{T} \]
  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 \( \Omega \) 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 \( R \ln \left( \frac{V_2}{V_1} \right) \); 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,

\[
y_i = \frac{n_i}{\sum_j n_j}
\]

always greater than zero, so mixing is spontaneous

- The probability form of the entropy, \(S = -k_B \sum_j p_j \ln p_j\) 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

\[
d\bar{S} = \bar{C}_V \frac{dT}{T} + R \frac{dV}{V}
\]

- The maximum efficiency of a (Carnot) engine is \( 1 - \frac{T_c}{T_h} \)
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