

STATISTICAL MOLECULAR THERMODYNAMICS

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Video 8.8

Review of Week 8

CRITICAL CONCEPTS FROM WEEK 8

- The Helmholtz free energy is defined as $A = U - TS$. At constant T and V , spontaneous processes occur to minimize A until the system is at equilibrium, at which point only reversible processes, for which $dA = 0$, occur.
- The Gibbs free energy is defined as $G = U + PV - TS$. At constant T and P , spontaneous processes occur to minimize G until the system is at equilibrium, at which point only reversible processes, for which $dG = 0$, occur.
- The maximum non- PV work that can be extracted from a spontaneous process occurring at constant T and V or constant T and P is ΔA and ΔG , respectively.
- Spontaneous free energy changes may depend on a balance of energetic and entropic changes.

CRITICAL CONCEPTS FROM WEEK 8

- Maxwell relations are determined through the equality of mixed partial derivatives of thermodynamic state functions with respect to other thermodynamic functions. An example deriving from A is

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

- Maxwell relations are useful for establishing a connection between thermodynamic state functions and PVT equations of state.
- An example of non- PV work is stretching a rubber band a length Δl against its restoring force f . More work is required at higher temperatures because the entropy of the rubber band decreases when it is stretched.

CRITICAL CONCEPTS FROM WEEK 8

- Natural independent variables for a given state function are those which permit derivatives of that state function with respect to those variables to be expressed as simple thermodynamic functions. For example the natural independent variables of H are S and P which leads to

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

- The Gibbs free energy of an ideal gas as a function of temperature and pressure can be related to the pressure and the standard molar Gibbs free energy at 1 bar using

$$\bar{G}(T,P) = G^\circ(T) + RT \ln P$$

CRITICAL CONCEPTS FROM WEEK 8

- The temperature dependence of the Gibbs free energy may be expressed through the Gibbs-Helmholtz equation

$$\left[\frac{\partial(G/T)}{\partial T} \right]_P = -\frac{H}{T^2}$$

- Gibbs free energy as a function of temperature may also be determined according to

$$\bar{G}(T) - \bar{H}(0) = \bar{H}(T) - \bar{H}(0) - T\bar{S}(T)$$

where the necessary enthalpy and entropy quantities may be determined from measured or computed constant pressure heat capacities integrated over relevant temperature changes and phase transitions.