

4 Engines and refrigerators

4.1 Heat Engines

See notes under 4.2

4.2 Refrigerators

- Efficiency and CoP, how they're defined and how the 1st and 2nd Law are used to relate them to temperatures.
- The efficiency of a Carnot Cycle
- Determining the Efficiency for specific cycles
 - Doing this when the 'working substance' is an ideal gas

4.3 Real Heat Engines

4.3.1 Internal Combustion Engines

- Determining the Efficiency of any given cycle by applying the 1st and 2nd Laws and, if the materials are ideal gases, explicit evaluations of the 1st law.

4.3.2 Steam Engines

- Using Enthalpies to determine efficiency
 - This uses that the enthalpies in the water are roughly equal and that the turbine doesn't change entropy, so the mixture of entropies is the same as the mixture of the enthalpies in the water + steam mixture.

4.4 Real Refrigerators

- Using enthalpies to determine efficiency

4.4.1 Throttling Process

- Throttling doesn't change enthalpy

4.4.2 Liquefaction of Gases

4.4.3 Toward Absolute Zero

5 Free Energy and Chemical Thermodynamics

5.1 Free Energy as Available Work

- Coming up with the available work (ΔG) or voltage generated through a chemical process such as that in
 - Electrolysis
 - Fuel cells
 - Batteries

5.1.1 Thermodynamic Identities

5.2 Free Energy as a Force toward Equilibrium

- Under what conditions is minimizing a system's Gibbs Free Energy equivalent to maximizing universal entropy?
- Ditto for Helmholtz Free Energy

5.2.1 Gibbs Free Energy and Chemical Potential

5.3 Phase Transformations of Pure Substances

5.3.1 Diamonds and Graphite

- The system of Pr. 5.29. Ask them to Plot G vs. P for the three phases given G, S and V data from the back of the book. They don't have to get the exact

transition pressures right, but should get slopes and values at atmospheric pressure.

5.3.2 *The Clausius-Clapeyron Relation*

- If two of these do intersect, then can ask them to give the slope of the equilibrium line in the P-T plane using eq'n 5.46.

5.3.3 *The van der Waals Model*

- Where do the extra terms come from?
- What can the van der Waals Model do that the Ideal Gas Model can't?
 - It spans liquids and gasses and shows the phase boundary including the critical point.

5.4 Phase Transformations of Mixtures

5.4.1 **Free Energy of Mixtures**

- How the interplay of the linear mixing of “unmixed” G^o 's, the Entropy of Mixing, and the energy of mixing leads to the formation of domains at moderate temperatures.
 - Be able to qualitatively generate the T vs. x plot from successive G vs. x plots for different temperatures.

5.4.2 **Phase Changes of a Miscible Mixture**

- How shifting G_{liquid} and G_{gas} for different temperatures gives rise to a T vs. x plot with a dead zone diagonally between the two species' pure boiling temperatures.
- What happens when you start with a gas of a given mixture, x, and lower the temperature, or, similarly if you start with a liquid and raise the temperature.

5.4.3 **Phase Changes of a Eutectic System**

- How shifting G_{liquid} and $G_{\text{solid } \alpha}$ and $G_{\text{solid } \beta}$ for different temperatures gives rise to a T vs. x plot with different phases of solid and a Eutectic point.

5.5 Dilute Solutions

5.5.1 **Solvent and Solute Chemical Potentials**

- Starting with

$$G \approx m_{\text{solvent}}(T, P)N_{\text{solvent}} + N_{\text{solute}}f(P, T) + N_{\text{solute}}kT \ln \left[\frac{N_{\text{solute}}}{N_{\text{solvent}}} \right] - N_{\text{solute}}kT,$$

show that $m_{\text{solvent}}(T, P) \approx m_{\text{solvent}}^o(T, P) - \frac{N_{\text{solute}}kT}{N_{\text{solvent}}}$ and

$$m_{\text{solute}} \approx f(P, T) + kT \ln \left[\frac{N_{\text{solute}}}{N_{\text{solvent}}} \right] = m_o(P, T) + kT \ln [M_{\text{solvent}}]$$

5.5.2 **Osmotic Pressure**

- Be able to use the solvent's chemical potential expression, with the help of a Taylor series, to find the Osmotic Pressure.

5.5.3 **Boiling and Freezing Points**

- Assuming that you have a dilute liquid that can either boil or freeze into a relatively pure form, the balance of chemical potentials leads to a relationship...
 - ...between the new equilibrium pressure (for given temperature) and the pressure at which the two phases would be in equilibrium if the liquid were pure. This is done by assuming the new pressure

is near the old pressure, so the pure chemical-potential expressions can be Taylor expanded in pressure.

- ...between the new equilibrium temperature (for given pressure) and the temperature at which two phases would be in equilibrium if the liquid were pure. This is done by assuming the new temperature is near the old temperature, so the pure chemical-potential expressions can be Taylor expanded in temperature.

5.6 Chemical Equilibrium

- The condition for equilibrium between reactants and products is that their chemical potentials balance, for example $2CO + O_2 \leftrightarrow 2CO_2$ requires

$$2m_{CO} + m_{O_2} = 2m_{CO_2}.$$

5.6.1 Nitrogen Fixation

- This is a case of three ideal gasses interacting, so $m(T, P) - m(T, P_o) = kT \ln(P/P_o)$ can be used to relate values of m (or G) tabulated for specific temperature and pressure to those at a different pressure.
- Thus the balance of chemical potentials can be rephrased in terms of the partial pressures of the reactants and products. In general terms, for a reaction $n_1X_1 + n_2X_2 + \dots \leftrightarrow a_1Y_1 + a_2Y_2 + \dots$ with X's being the reactants,

and Y's being the products,
$$K \equiv e^{-\Delta G^\circ / RT} = \frac{\left(\left(\frac{P_{Y_1}}{P_o} \right)^{a_1} \left(\frac{P_{Y_2}}{P_o} \right)^{a_2} \dots \right)}{\left(\left(\frac{P_{X_1}}{P_o} \right)^{n_1} \left(\frac{P_{X_2}}{P_o} \right)^{n_2} \dots \right)}$$
 where P_o

is the reference pressure at which G° 's were evaluated, and

$$\Delta G^\circ = (a_1 \Delta G(T, P_o)_{f.Y_1} + a_2 \Delta G(T, P_o)_{f.Y_2} + \dots) - (n_1 \Delta G(T, P_o)_{f.X_1} + n_2 \Delta G(T, P_o)_{f.X_2} + \dots)$$

5.6.2 Dissociation of Water

- This is a case of a dilute solution of H^+ and OH^- in H_2O , so the chemical potential relationship can be phrased in terms of molalities.

$$m_{H_2O}^\circ = (m_{H^+}^\circ + kT \ln m_{H^+}) + (m_{HO^-}^\circ + kT \ln m_{HO^-}).$$
 Rearranging gives

$$m_{H^+} m_{HO^-} = e^{-\Delta G^\circ / RT}.$$

- $pH \equiv -\log_{10} m_{H^+}$
- More generally, if you have a reaction in which all members are solutes in a dilute solution, then reaction $n_1X_1 + n_2X_2 + \dots \leftrightarrow a_1Y_1 + a_2Y_2 + \dots$ leads

$$\text{to } \frac{(m_{Y_1})^{a_1} (m_{Y_2})^{a_2} \dots}{(m_{X_1})^{n_1} (m_{X_2})^{n_2} \dots} = e^{-\Delta G^\circ / RT} = K$$

5.6.3 Oxygen Dissolving in Water

- This puts into balance an ideal gas on one side and a dilute solute on the other, so the balance of chemical potentials becomes

$\mathbf{m}^{\circ}_{O_{2,g}} + kT \ln(P / P^{\circ}) = \mathbf{m}^{\circ}_{O_{2,aq}} + kT \ln m_{O_2}$ which rearranges to

$$\left(\frac{P^{\circ} m_{O_2}}{P} \right) = e^{-\Delta G^{\circ} / RT} = K$$

5.6.4 Ionization of Hydrogen

- This is a balance of ideal gasses, but with ionization energy.