Chapter 8

Thermodynamic Relations

8.1 Types of Thermodynamic Properties

The thermodynamic state of a system can be characterized by its properties that can be classified as measured, fundamental, or derived properties. We want to develop relationships to relate the changes in the fundamental and derived properties in terms of the measured properties that are directly accessible from laboratory measurements. Some of the measured properties are \( P, v, T, \) composition, \( c_p, \) and \( c_v. \) The small letters are used to denote specific quantities for example \( v \) is specific volume.

The fundamental properties are internal energy \( u \) and entropy \( s. \) These properties arrive from the first and second law of thermodynamics. The first law states that energy is conserved, and the second law states that entropy of the universe always increases.

The derived properties are defined to facilitate the energy balance of systems in which the combination of internal energy and other properties often occurs. In open systems, the mass that crosses the boundary between the surroundings and the system always contributes to two terms in the energy balance: internal energy and flow work \((Pv).\) For convenient we can define an enthalpy \((h)\) as

\[
h = u + Pv
\]

In terms of the total enthalpy \( H, \) we have

\[
H = U + PV
\]

We can then make an enthalpy balance for an open system in which the flow work is included in the enthalpy term. Figure 8.1-1 shows a raindrop created from the surrounding super saturated vapor in the atmosphere. Not only the energy \( U \) of the raindrop is needed but also some additional energy, equal to \( PV, \) is required to push the atmosphere out of the way to make room for the drop.

![Figure 8.1-1 An energy of \( U + PV \) is required to create a raindrop.](image)

Enthalpy is the total energy we would need, to create a system out of nothing and put it in an environment with constant pressure \( P. \) Or, if we could completely annihilate a system, \( H \) is
the energy we could recover: the system’s energy plus the work done by the collapsing atmosphere.

However, we usually are not interested in the total energy needed or the total energy that can be recovered from a system. We will be more interested in the work involved in a system. For isothermal surroundings, the system can extract heat from the surroundings for free, so the work required to create the system from nothing is equal to the internal energy minus the heat received. And if we annihilate the system, we generally cannot recover all its energy as work since we have to dispose of its entropy by dumping some heat into the surroundings. Therefore it is more convenient to define the Helmholtz free energy, $A$, for an environment at constant temperature $T$

$$A = U - TS \quad (8.1-2)$$

$A$ is the energy that must be provided as work if we create the system out of nothing. The heat extracted from the surroundings is $T\Delta S = T(S_f - S_i) = TS_f$ where $S_f$ is the system final entropy and $S_i$ the system zero initial entropy. If we annihilate a system with initial entropy $S_i$, $A$ is the amount of recovered work, since we have to dump some heat, equal to $TS_i$, into the environment to get rid of the system’s entropy.

Equation (8.1-2) includes all work, even the work done by the system’s surroundings. If the system is in an isothermal and isobaric environment, it is more convenient to use the Gibbs free energy

$$G = U - TS + PV \quad (8.1-3)$$

Gibbs free energy is the work required to create a system from nothing in an environment with constant $P$ and constant temperature $T$.

We usually are more interested in the change in states of a system rather than its creation or annihilation. We then want to look at the changes in $A$ and $G$. The change in $A$ at constant temperature is given by

$$\Delta A = \Delta U - T\Delta S = Q + W - T\Delta S \quad (8.1-4)$$

In this expression $Q$ is the heat added and $W$ is the work done on the system. If the process is reversible then $Q = T\Delta S$ and the change in $A$ is precisely equal to the work done on the system. If the process is irreversible then $Q < T\Delta S$ and $\Delta A < W$, the change in $A$ is less than the work done on the system.

For an environment with constant $P$ and constant temperature $T$, the change in $G$ is given by

$$\Delta G = \Delta U - T\Delta S + P\Delta V = Q + W - T\Delta S + P\Delta V \quad (8.1-5)$$

For any process we have

$$Q - T\Delta S \leq 0 \text{ (equal sign for reversible processes)} \quad (8.1-6)$$
The work term $W$ consists of the work done by the environment, $-P\Delta V$, and any “other” work done on the system.

$$W = -P\Delta V + W_{\text{other}}$$  \hspace{1cm} (8.1-7)

Substituting equations (8.1-6) and (8.1-7) into equation (8.1-5) we obtain

$$\Delta G \leq W_{\text{other}} \text{ at constant } T, P$$  \hspace{1cm} (8.1-8)

**Example 8.1-1.**

Determine the electrical work required to produce one mole of hydrogen in the electrolysis of liquid water at 298°FK and 1 atm. The chemical reaction is

$$\text{H}_2\text{O}(l) \rightarrow \text{H}_2(g) + 0.5\text{O}_2(g)$$

Data (at 298°FK and 1 atm): $\Delta H = 286$ kJ for this reaction, $S_{\text{H}_2\text{O}} = 70$ J/°K, $S_{\text{H}_2} = 131$ J/°K, and $S_{\text{O}_2} = 205$ J/°K.

**Solution**

$$G = H - TS$$

At constant $T$ we have

$$\Delta G = \Delta H - T\Delta S$$

The change in system entropy is given by

$$\Delta S = S_{\text{H}_2} + 0.5S_{\text{O}_2} - S_{\text{H}_2\text{O}} = 131 + 0.5(205) - 70 = 163.5 \text{ J/°K}$$

The change in $G$ is then

$$\Delta G = 286 \text{ kJ} - (298°FK)(163.5 \text{ J/°K}) = 237 \text{ kJ}$$

This is the amount of energy in terms of electrical work required to produce one mole of hydrogen by electrolysis.

If we burn one mole of hydrogen, the amount of heat we would get is 286 kJ. If we can combine one mole of hydrogen and half a mole of oxygen in a fuel cell to produce water we can extract 237 kJ of electrical work. The difference $\Delta H - \Delta G = T\Delta S = 49$ kJ is the waste heat that must be expelled by the fuel cell to get rid of the excess entropy that was in the gases. Therefore the maximum efficiency, $\varepsilon_{\text{fuel cell}}$, of the fuel cell is

$$\varepsilon_{\text{fuel cell}} = 237/286 = 0.829$$

This efficiency is higher than the 40% efficiency of electrical power plants.
Example 8.1-2.  

In a hydrogen fuel cell shown in Figure 8.1-2, hydrogen and oxygen gas pass through porous electrodes and react to form water. Electrons are released at the anode (negative electrode) and deposited at the cathode (positive electrode). The overall reaction is

$$\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$$

Calculate the voltage of the cell.

Data (at 298°K and 1 atm): $\Delta G = - 237 \text{ kJ}$ for this reaction.

![Figure 8.1-2 A hydrogen fuel cell](image)

Solution

In a hydrogen fuel cell\(^1\), the steps of the chemical reaction are

$$\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2e^- \text{ (at } - \text{ electrode)}$$

$$0.5\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- \text{ (at } + \text{ electrode)}$$

Two electrons are pushed through the circuit each time the full reaction occurs. The electrical work produced per electron is

$$237 \text{ kJ}/(2 \times 6.02 \times 10^{23}) = 1.97 \times 10^{-19} \text{ J} = 1.23 \text{ eV}$$

(Note: 1 eV = 1.602 $\times 10^{-19}$ J)

Since 1 volt is the voltage needed to give each electron 1 eV of energy, so the fuel cell has a voltage of 1.23 V.

**8.2 Equations of State**

In the calculations of energy, enthalpy, and entropy of a substance we need an accurate representation of the relationship among pressure, volume, and temperature. Besides the tabular and graphical presentations of the \( p-v-T \) relationship, analytical formulations, called *equation of state*, constitute another way of expressing the \( p-v-T \) relationship. The equations of state are convenient for performing the mathematical operations required to calculate \( u, h, s \), and other thermodynamic properties.

In chapter 3 we mention the compressibility factor, the virial, and the Soave-Redlick-Kwong equation of states. The virial equation of state can be derived from the principle of statical mechanics to relate the \( p-v-T \) behavior of a gas to the forces between molecules. A virial equation of state expresses the quantity \( \frac{p\bar{v}}{RT} \) as a power series in the inverse of molar volume \( \bar{v} \).

\[
Z = \frac{p\bar{v}}{RT} = 1 + \frac{B(T)}{\bar{v}} + \frac{C(T)}{\bar{v}^2} + \frac{D(T)}{\bar{v}^3} + \ldots \tag{8.2-1}
\]

In this equation, \( B, C, \) and \( D \) are called *virial coefficient* and are functions of temperature. For a truncated virial equation with two terms we have

\[
\frac{p\bar{v}}{RT} = 1 + \frac{B(T)}{\bar{v}} \tag{8.2-2}
\]

In this equation, \( B(T) \) can be estimated from the following equations:

\[
B(T) = \frac{\bar{R}T_c}{p_c} (B_0 + \omega B_1) \tag{8.2-3}
\]

\[
B_0 = 0.083 - \frac{0.422}{T_R^{1.6}}, \quad B_1 = 0.139 - \frac{0.172}{T_R^{4.2}}
\]

In equation (8.2-3), \( \omega \) is the Pitzer acentric factor, which is a parameter reflecting the geometry and polarity of a molecule. The acentric factor for over 1000 compounds can be obtained from *comp4.exe* program written by T.K. Nguyen. This program is available in the Distribution Folder for CHE302 course. In the limiting case where there are no interactions between the molecules, all the virial coefficients are equal to zero. Eq. (8.2-1) becomes

\[
Z = \frac{p\bar{v}}{RT} = 1 \tag{8.2-4}
\]

Eq. (8.2-4) is the ideal gas equation of state. We will use the Van de Walls equation of state to illustrate the evaluation of thermodynamic properties. Both the Van de Walls and the SRK equations of state have two adjustable constants but the Van de Walls equation is simpler. The Van de Walls equation of state is
In this equation, the constant $b$ accounts for the finite volume occupied by the molecules and the term $\frac{a}{\bar{v}^2}$ accounts for the attractive forces between molecules.

The Van der Waals parameters $a$ and $b$ can be determined from the critical properties since there is an inflection point at the critical isotherm as shown in Figure 8.2-1. At the critical point we have

\[
\left(\frac{\partial P}{\partial \bar{v}}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial \bar{v}^2}\right)_{T_c} = 0 \tag{8.2-6}
\]

The isotherm passing through the critical point is given by

\[ P = \frac{\bar{R}T_c}{\bar{v} - b} - \frac{a}{\bar{v}^2} \]

The first and second derivatives of $P$ with respect to $\bar{v}$ are given by

\[
\left(\frac{\partial P}{\partial \bar{v}}\right)_{T_c} = -\frac{\bar{R}T_c}{(v_c - b)^2} + \frac{2a}{v_c^3} = 0 \tag{8.2-6a}
\]

\[
\left(\frac{\partial^2 P}{\partial \bar{v}^2}\right)_{T_c} = \frac{2\bar{R}T_c}{(v_c - b)^3} - \frac{6a}{v_c^4} = 0 \tag{8.2-6b}
\]

We can solve the two equations (8.2-6a) and (8.2-6b) for the two unknowns $a$ and $b$. Multiplying equation (8.2-6a) by 2 and equation (8.2-6b) by $(\bar{v}_c - b)$ and add them together we get

\[
8-6
\]
\[
\frac{4a}{V_c^3} - \frac{6a}{V_c^5}(\bar{V}_c - b) = 0
\]  
(8.2-7)

\[
4a\bar{V}_c - 6aV_c + 6ab = 0 \Rightarrow \bar{V}_c = 3b
\]  
(8.2-8)

Substituting \( b = \bar{V}_c / 3 \) into equation (8.2-6a) and solving for \( a \) gives

\[
a = \frac{9}{8} \bar{V}_c \bar{R} T_c
\]

At the critical point we have

\[
P_c = \frac{\bar{R}T_c}{\bar{V}_c - b} - \frac{a}{\bar{V}_c^2}
\]  
(8.2-9)

We can use equation (8.2-9) to solve for \( \bar{V}_c \) in terms of critical temperature and critical pressure. Substituting \( a = \frac{9}{8} \bar{V}_c \bar{R} T_c \) and \( b = \bar{V}_c / 3 \) into equation (8.2-9) we obtain

\[
P_c = \frac{3\bar{R}T_c}{2\bar{V}_c} - \frac{9\bar{V}_c \bar{R} T_c}{8\bar{V}_c^3} = \frac{3\bar{R}T_c}{2\bar{V}_c} \left( \frac{3}{2} - \frac{9}{8} \right) = \frac{3\bar{R}T_c}{8\bar{V}_c}
\]

Solving for \( \bar{V}_c \) in terms of \( P_c \) and \( T_c \) we have

\[
\bar{V}_c = \frac{3\bar{R}T_c}{8P_c}
\]

Hence

\[
a = \frac{9}{8} \bar{V}_c \bar{R} T_c = \frac{27}{64} \left( \bar{R} T_c \right)^2 \frac{1}{P_c}
\]

Using \( \bar{R} = 8.314 \text{ J/(mol} \cdot \text{K}) = 8.314 \times 10^{-5} \text{ m}^3\text{bar/(mol} \cdot \text{K}) \) and for propane, \( T_c = 369.9 \text{K}, P_c = 42.46 \text{ bar} \), we have

\[
a = \frac{27}{64} \frac{(\bar{R} T_c)^2}{P_c} = \frac{27}{64} \frac{(8.314 \times 10^{-5} \times 369.9)^2}{42.46} = 9.36 \times 10^{-6} \text{ m}^6\text{bar/mol}
\]
Example 8.2-1.\(^2\)

For the Van Der Waals isotherm shown in the following figure, show that the saturation pressure can be determined by locating the horizontal, two-phase segment of the isotherm so that two equal areas are enclosed between it and the Van de Waals curve.

![Van Der Waals isotherm diagram]

Solution

From the grouping \{G, T, P\}, we have \(G = G(T, P)\), therefore

\[
dG = \left(\frac{\partial G}{\partial T}\right)_P \, dT + \left(\frac{\partial G}{\partial P}\right)_T \, dP = -S \, dT + V \, dP
\]

Along an isotherm of the equation of state, \(dT = 0\), therefore \(\Delta G = \int_{P_a}^{P_b} V \, dP\)

At the saturation pressure \(\Delta G = G^V - G^L = 0\), we have

\[
\Delta G = G^V - G^L = \int_{P_a}^{P_b} V \, dP + \int_{P_a}^{P_f} V \, dP + \int_{P_f}^{P_v} V \, dP + \int_{P_v}^{P_b} V \, dP = 0
\]

Since area (1) = \(-\int_{P_a}^{P_v} V \, dP - \int_{P_b}^{P_f} V \, dP\), and area (2) = \(\int_{P_f}^{P_v} V \, dP + \int_{P_v}^{P_b} V \, dP\), the saturation pressure can be determined by locating the horizontal, two-phase segment of the isotherm so that two equal areas are enclosed between it and the Van Der Waals curve.

\(^2\) Kyle, B.G., Chemical and Process Thermodynamics, Prentice Hall, 1999