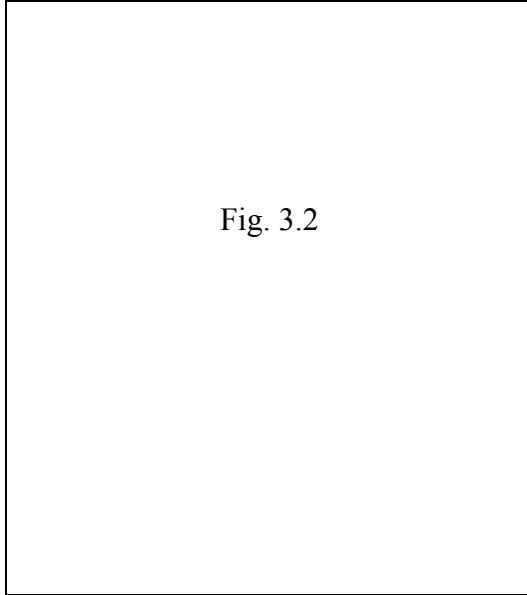# CHAPTER 3 LECTURE NOTES

3.1. The Carnot Cycle

Fig. 3.2

Consider the following reversible cyclic process involving one mole of an ideal gas:

(a) Isothermal expansion from (P_1,V_1,T_h) to (P_2,V_2,T_h),

(b) Adiabatic expansion from (P_2,V_2,T_h) to (P_3,V_3,T_c),

(c) Isothermal compression from (P_3,V_3,T_c) to (P_4,V_4,T_c),

(d) Adiabatic compression from (P_4,V_4,T_c) back to (P_1,V_1,T_h).

Table 3.1 provides a summary of the changes in ΔU, q_{rev}, and w_{rev} during this process.

During the expansion phase of the cycle, the system absorbs an amount of heat equal to

$$q_{A\to C} = RT_h \ln\left(\frac{V_2}{V_1}\right) + 0,$$

and performs an amount of work equal to

$$w_{A\to C} = RT_h \ln\left(\frac{V_1}{V_2}\right) + C_{V,m}(T_c - T_h)$$

During the compression phase, the system gives out an amount of heat equal to

$$q_{C\to A} = RT_c \ln\left(\frac{V_4}{V_3}\right) + 0,$$

and the surroundings perform an amount of work on the system equal to

$$w_{C\to A} = RT_c \ln\left(\frac{V_3}{V_4}\right) + C_{V,m}(T_h - T_c)$$

Using the equation derived for adiabats, we can show (see Eq. 3.15) that

$$\frac{V_4}{V_3} = \frac{V_1}{V_2}. \tag{3.16}$$

Therefore, for the cyclic process, we have:

$$\text{net heat} = q_{rev} = R(T_h - T_c) \ln\left(\frac{V_2}{V_1}\right) \tag{3.18}$$

Since $T_h > T_c$ and $V_2 > V_1$, $q_{rev} > 0$. Therefore, heat is <u>absorbed</u> at the higher temperature during each cycle.

$$\text{net work} = w_{rev} = R(T_h - T_c) \ln\left(\frac{V_1}{V_2}\right) \tag{3.19}$$

Since $T_h > T_c$ and $V_2 > V_1$, $w_{rev} < 0$. Therefore, <u>work is done by the system</u> during each cycle.

The Carnot Cycle, therefore, is a mechanism whereby some heat from the high temperature heat source is transferred to a low temperature heat sink and in the process, some work is done by the system. The efficiency of an engine is the ratio of the work done to the amount of heat absorbed, i.e.,

$$\in = \frac{|w_{rev}|}{q_{A \to B}} = \frac{R(T_h - T_c) \ln(V_2/V_1)}{RT_h \ln(V_2/V_1)} \tag{3.20}$$

where, in order to get physically meaningful values for efficiency, we have made the numerical value of w_{rev} positive. This yields

$$\in = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h} \tag{3.21}$$

Therefore, *the efficiency depends only on the temperatures of the heat source and the heat sink and has no dependence on the working fluid of the engine* .

Example 3.1, Problems 3.1–3.5

Entropy:

We may also write the right hand side of Eq. (3.20) as follows:

$$\in = \frac{q_{A \to B} + q_{C \to D}}{q_{A \to B}} = \frac{q_h + q_c}{q_h}.$$

This gives $\in = 1 + \dfrac{q_c}{q_h} = 1 - \dfrac{T_c}{T_h}$ i.e., $\dfrac{q_c}{q_h} = -\dfrac{T_c}{T_h}$ or $\dfrac{q_h}{T_h} + \dfrac{q_c}{T_c} = 0$ (3.28)

This last relationship suggests that q/T is a state property, adding up to zero for the whole cyclic process. This property is called **entropy change of the system**, and is <u>formally</u> defined as

$$dS = \frac{dq_{rev}}{T}.$$

Reading Assignment: Sections 3.2 (Clausius statement of the second law), 3.3.

3.4. Calculation of Entropy Changes

The Clausius statement requires that the entropy of the Universe increase during every actual (i.e., irreversible) process. Entropy change of the system, dS (or ΔS) is a state property, independent of the path taken by the process. On the other hand, entropy change of the surroundings, dS_{surr} (or ΔS_{surr}) explicitly depends on the path. We need both of these quantities in order to determine the entropy change of the Universe during a process:

$$dS_{univ} = dS + dS_{surr} \text{ or } \Delta S_{univ} = \Delta S + \Delta S_{surr}.$$

Therefore, in calculations of entropy changes for real processes, we take the following strategy:

(a) Entropy change of the system is always calculated using a reversible path, which we may have to construct, connecting the initial and final states.

(b) Entropy change of the surroundings is always calculated using the <u>actual</u> process in consideration.

<u>Types of processes:</u>

1. Phase changes: $\Delta S_{pc} = \dfrac{\Delta_{pc}H}{T_{pc}}$.

    Problems: 3.7, 3.17, 3.25, 3.30, 3.31, 3.35

2. Mixing : $\Delta S_{mix} = -R \sum_i x_i \ln x_i$.

    Problems: 3.12, 3.13

3. Heating or cooling at constant pressure or constant volume (one mole):

    $$\Delta S = \int_{T_1}^{T_2} \frac{C_{P,m}}{T} dT \text{ or } \int_{T_1}^{T_2} \frac{C_{V,m}}{T} dT.$$

    Example 3.2, Problems: 3.11, 3.17, 3.23, 3.25, 3.30, 3.31, 3.33, 3.35

4. Isothermal expansion/compression (ideal gas):

    $$\Delta S = \int_{V_1}^{V_2} \frac{P}{T} dV = nR \ln\left(\frac{V_2}{V_1}\right) = nR \ln\left(\frac{P_1}{P_2}\right)$$

    Problems: 3.16, 3.17, 3.20, 3.24, 3.33

5. Entropy change during an adiabatic process = 0 by definition!

6. Entropy of reaction/formation:

    $$\sum_{products} n_i S^o_{f,i} - \sum_{reactants} n_j S^o_{f,j}$$

    The absolute entropies $S°$ appearing in this equation are obtained using the Third Law of Thermodynamics.

Problems: 3.10, 3.11, 3.15

The Third Law of Thermodynamics

The entropy of a pure, perfectly crystalline solid at absolute zero temperature is zero.

In other words, for a perfectly crystalline substance,

$$\lim_{T \to 0} S = \lim_{T \to 0} \frac{q_{rev}}{T} = 0$$

This gives us a way to calculate the absolute entropy S (as opposed to entropy chages, ΔS) for a pure substance at any temperature. So, for example, if we wished to find the absolute entropy of water at 800 K, we would write (formally):

$$S_{800} = \int_0^{273.15} \frac{C_{P,H_2O(s)}}{T} dT + \frac{\Delta_{fus}H}{273.15} + \int_{273.15}^{373.15} \frac{C_{P,H_2O(l)}}{T} dT + \frac{\Delta_{vap}H}{273.15}$$
$$+ \int_{373.15}^{800} \frac{C_{P,H_2O(g)}}{T} dT.$$

In practice, the first term cannot be evaluated. So, calculations of absolute entropy depend on the experimentally determined absolute entropy at some low temperature. If this value is given, say S at 10 K, denoted as S_{10}, the first term can be replaced by
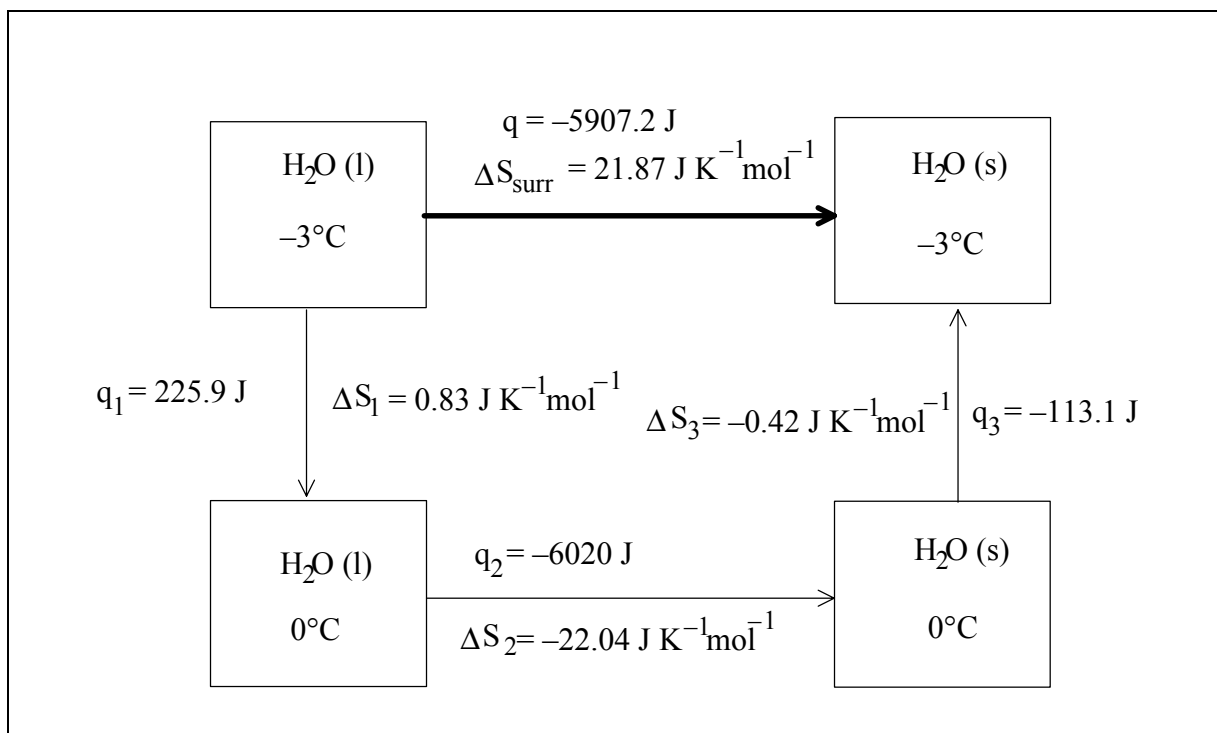
$$\int_0^{273.15} \frac{C_{P,H_2O(s)}}{T} dT = S_{10} + \int_{10}^{273.15} \frac{C_{P,H_2O(s)}}{T} dT.$$

Depending on the problem at hand, some or all of the terms in these expressions may have to be used.

Problems: 3.36, 3.47

3.6. Conditions for Equilibrium

Problem 3.25:

The entropy change for the system:

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -21.63 \text{ J K}^{-1}\text{mol}^{-1}$$

Entropy change for the surroundings:

$$\Delta S_{surr} = \frac{5907.2 \text{ J mol}^{-1}}{270.15 \text{ K}} = 21.87 \text{ J K}^{-1}\text{mol}^{-1}$$

Therefore, $\Delta S_{univ} = +0.24$ J K^{-1} mol^{-1}.

Calculating entropy changes of the surroundings is not always possible. Therefore, it is desirable to have a criterion for spontaneity that depends ONLY on system variables.

Constant Pressure and Temperature Processes:

In Problem 3.25, the actual enthalpy change during the process is -5907.2 J mol^{-1}. This is the heat lost from the system and gained by the surroundings.

Therefore, in this case, we have

$$\Delta H - T\Delta S = -5907.2 \text{ J mol}^{-1} - 270.15 \text{ K}(-21.63 \text{ J K}^{-1}\text{mol}^{-1})$$

$$= -63.86 \text{ J mol}^{-1}.$$

The quantity $H - TS$ is defined as Gibbs Free Energy, G, which is always negative for a spontaneous (irreversible) process taking place at constant temperature and pressure.

Thus, by definition, $G = H - TS$,

$$dG = dH - TdS \text{ at constant temperature}$$

$$dG < 0 \text{ for irreversible processes at constant } T \text{ and } P.$$

$$dG = 0 \text{ for reversible (equilibrium) processes at constant } T \text{ \& } P.$$

Constant Volume and Temperature Processes:

For constant volume, isothermal processes, it can be shown that a similar state property can be defined as $A = U - TS$,

$$dA = dU - TdS \text{ at constant temperature}$$

$$dA < 0 \text{ for irreversible processes at constant } T \text{ and } V.$$

$$dA = 0 \text{ for reversible (equilibrium) processes at constant } T \text{ \& } V.$$

The state property A is called the Helmhotz Free Energy.

Reactions:

Gibbs energies of formation can be used in the same way as enthalpies of formation to determine ΔG of reactions.

Isothermal Reversible Expansion/Compression of an Ideal Gas:

$$w_{rev} = nRT\ln\left(\frac{V_1}{V_2}\right) = nRT\ln\left(\frac{P_2}{P_1}\right).$$

$$q_{rev} = T\Delta S = -w_{rev}, \text{ since } \Delta U = 0.$$

$$\Delta H = 0 \text{ (ideal gas)}.$$

Therefore, for an isothermal reveresible expansion/compression of an ideal gas,

$$\Delta G = \Delta H - T\Delta S = w_{rev} = nRT\ln\left(\frac{P_2}{P_1}\right)$$

Problems: 3.37, 3.38, 3.40, 3.41, 3.42, 3.43, 3.48 – 3.52, 3.54, 3.55.

3.8. Maxwell's Relations:

Maxwell's relations are derived using a very predictable and systematic four step procedure:

Step 1: Derive the "parent expression" for the state property of interest:

Eg. $dU = dq + dw = TdS - PdV$.

Step 2: Express the same differential using the chain rule of partial differentiation:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV.$$

Step 3: Equate terms containing the same differential between these two equations to get

$$\left(\frac{\partial U}{\partial S}\right)_V = T \text{ and } \left(\frac{\partial U}{\partial V}\right)_S = -P$$

Step 4: Use Euler's theorem for exact differentials (the order of differentiation is immaterial)

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V, \text{which gives}$$

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

This last equation is one of the four **Maxwell's Relations**. Similar relations can be derived from dH, dA, and dG. These give (Steps 3 and 4) the relations shown on p. 128 (Eq. 3.116 – 3.119) and p. 129 (Eq. 3.122 – 3.125).

Problem: 3.63.

Thermodynamic Equations of State:

Consider

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V \tag{3.128}$$

We define two quantities of great importance and usefulness:

Cubic expansion coefficient:

$$a = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{3.139}$$

This is a measure of the increase in volume with an increase in temperature, and may also be called *thermal expansivity* or *thermal expansion coefficient*.

Isothermal compressibility:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

The negative sign indicates that volume decreases as pressure is increased, which is the behavior observed for nearly all substances including solids and liquids.

Using these two definitions, and using the relationship that

$$\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V = -1, \tag{C.11}$$

we can re-write the thermodynamic equation of state Eq. (3.128) as

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{aT - \kappa P}{\kappa},$$

which is a <u>completely</u> <u>general</u> <u>expression</u> <u>applicable</u> <u>to</u> **all** <u>substances</u>.

Problems: 3.62 – 3.64.

3.9. Gibbs Helmholz Equation

See p. 135 of Text.

Connection to experiments 1 and 5 in the P. Chem. Lab:

Recall (from Chem 102) that $\Delta G° = -RT \ln K_{eq}$.

Substitute for $\Delta G°/T$ in Eq. (3.168) to get

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta G°}{T} \right) \right]_P = \frac{\partial}{\partial T}\left(-R \ln K_{eq} \right) = -\frac{\Delta H°}{T^2}, \text{ or}$$

$$\frac{\partial}{\partial T} \ln K_{eq} = \frac{\Delta H°}{RT^2}.$$

Rearranging, we get

$$d \ln K_{eq} = \frac{\Delta H°}{RT^2} dT,$$

which, when integrated, yields

$$\ln K_{eq} = -\frac{\Delta H°}{RT} + c$$

In Expt. 1, the equilibrium is a heterogeneous equilibrium between a liquid and its vapor.

In Expt. 5, the equilibrium is a homogeneous equilibrium between acetic acid and its dissociation products.

Problems: 3.42, 3.45, 3.46.

Fugacity:

Since, from Eq. (3.115), $dG = VdP - SdT$, for an isothermal process, we have

$$\Delta G = \int_{P_1}^{P_2} VdP.$$

For ideal gas, we can substitute for V and obtain

$$\Delta G = nRT\ln\left(\frac{P_2}{P_1}\right),$$

or with reference to a standard pressure, $P°$, we may write

$$G - G° = nRT\ln\left(\frac{P}{P°}\right), \text{or}$$

$$G_m = G_m° + RT\ln\left(\frac{P}{P°}\right).$$

Now, consider a real gas that obeys the equation of state

$$(P + a)(V_m - b) = RT,$$

which would give

$$G_m = G_m° + RT\ln\left(\frac{P+a}{P° + a}\right) - b(P - P°)$$

More complicated equations of state will give rise to more complicated expressions for ΔG.

In order to preserve the simplicity of the expression for ΔG even for real gases, the concept of **fugacity**, f, was introduced by G.N. Lewis so that

$$G_m = G_m° + RT\ln\left(\frac{f}{P°}\right)$$

with the condition that

$$\lim_{P\to 0} \frac{f}{P} = 1$$

A working expression to calculate fugacity:

For a constant temperature process, $dG_m = V_m dP$, or

$$\Delta G_m = G_{2,m} - G_{1,m} = \int_{P_1}^{P_2} V_m dP. \tag{3.154}$$

Let us add and subtract RT/P to the right hand side:

$$\Delta G_m = \int_{P_1}^{P_2} \left[\frac{RT}{P} + \left(V_m - \frac{RT}{P} \right) \right] dP$$
$$= RT \ln\left(\frac{P_2}{P_1} \right) + \int_{P_1}^{P_2} \left(V_m - \frac{RT}{P} \right) d \qquad (3.155, 3.156)$$

Now, *by definition*, for all gases, $\Delta G_m = RT\ln(f_2/f_1)$. Therefore, we get

$$RT \ln \frac{f_2/P_2}{f_1/P_1} = \int_{P_1}^{P_2} \left(V_m - \frac{RT}{P} \right) dP \tag{3.158}$$

We now set $P_1 = 0$ (recall that $f = P$ as $P \rightarrow 0$), $f_2 = f$ and $P_2 = P$, where P is the pressure of interest, to get

$$RT \ln\left(\frac{f}{P} \right) = \int_0^P \left(V_m - \frac{RT}{P} \right) dP$$

The right hand side can be evaluated if V_m can be conveniently expressed as a function of R, T and P. However, this is often very difficult (consider the van der Waals equation of state, for example). An alternative is to express V_m in terms of the compressibility factor Z,

$$V_m = ZRT/P,$$

to get

$$RT \ln\left(\frac{f}{P} \right) = \int_0^P \left(\frac{ZRT}{P} - \frac{RT}{P} \right) dP, \text{ or}$$
$$\ln\left(\frac{f}{P} \right) = \int_0^P \left(\frac{Z-1}{P} \right) dP.$$

The last expression can be conveniently and fairly accurately evaluated in most cases using Virial expansions.

Problems: 3.71, 3.72.