

Exploring Thermodynamics

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II. Thermo-chemistry

1. Introduction. In chapter I. Thermo-Physics, the basic concepts of heat, work, and internal energy were explained along with their relationship to each other. Basic reversible processes, applied to an ideal gas were also examined in some detail. The state variable entropy was defined, and the state functions of Enthalpy, Helmholtz energy, and Gibbs energy were derived. Since virtually all of the above concepts are unfamiliar to most individuals, general discussion with the intent of answering questions of “meaning” and “usefulness” was provided.

In chapter II. Thermo-Chemistry, we turn our attentions to some areas of chemistry for which the concepts discussed in I. Thermo-Physics become useful. Questions such as: 1) What heat is evolved in a reaction?, 2) Will this reaction proceed spontaneously?, 3) Has this system reached chemical equilibrium?, will be answered.

Most of the situations encountered in chemistry involve reactions carried out under constant pressure. This is because the reaction vessel is usually open to the atmosphere. Under the condition of constant pressure, the state function Enthalpy is most useful. Recall that the change in Enthalpy, under constant pressure conditions, may be interpreted as heat,

$$\Delta H = \Delta U + \Delta(PV) = \int TdS + \int VdP = \int TdS = Q_{Heat} ,$$

since $dP=0$ under constant pressure.

Chemists often refer to the change in enthalpy of a reaction, as the “heat of the reaction” for this reason.

The state function Gibbs free energy is also very useful in chemistry. Recall this function was defined, in Chapter I. Thermo-Physics, as:

$$\Delta G \equiv \Delta H - \Delta(TS) \equiv \Delta U + \Delta(PV) - \Delta(TS) = -\int SdT + \int VdP$$

and for a constant temperature process, ΔG represents [negative net work] for the process. When a system is not in equilibrium, it has available energy (or what is often called *FREE* energy) to do work. In moving toward equilibrium, the system releases this energy in the form of work as it lowers its energy state. In chemical systems open to the atmosphere, this is usually PV work. Thus, for a constant pressure chemical reaction, if $\Delta G < 0$, the reaction is spontaneous; and if $\Delta G = 0$, the reaction is in equilibrium.

2. State variables, State Functions, in Standard State. To proceed, a basis for information tabulation is adopted. With the understanding that absolute numerical values of state functions are impossible to obtain, AND, since we are only concerned with changes in these functions, the field of Thermo-Chemistry has decided to *assign* values to these state functions in an effort to create a basis for information tabulation and problem computation.

A symbolic notation has also been adopted by the field of thermo-chemistry. A zero superscript is placed on the thermodynamic quantity to indicate that the pressure is at standard state, X^0 . A bar is placed over the quantity to indicate that it is “per mole” or “molar” in value. A subscript is included to indicate the Kelvin temperature at which the thermodynamic quantity is valid. For example, \bar{H}_{298}^0 refers to a molar enthalpy at 1 atmosphere, and 298 K.

We thus define the Standard State. The standard value of the environmental state variables, pressure and temperature, are (by choice):

- Standard pressure is defined as 1 atmosphere.
- Standard temperature is defined as 298.15 K (25 C).
- Entropy, also a state variable, was earlier introduced as a measure of disorder. It is argued that (based on mixing, configuration, and velocity entropy) a minimum state of disorder for a material would exist under the conditions: a pure, well ordered crystal, at 0 K. Thus, a material under these conditions is assigned an absolute entropy value of ZERO.

$$S_{0K}^0 \equiv 0.$$

Entropy values at other temperatures are computed from thermodynamic data (see I. Thermo-Physics, sec 14). For example:

$$dS = \frac{1}{T} dq_{rev}$$

$$\int_{S_0}^{S_{298}} dS = \int_{0K}^{298K} \frac{1}{T} dq_{rev}$$

$$S_{298K}^0 - S_{0K}^0 = \int_{0K}^{298K} \frac{nC_p}{T} dT \quad (\text{for a 1 atm constant pressure})$$

$$S_{298K}^0 - 0 = \int_{0K}^{298K} \frac{nC_p}{T} dT \equiv S_{298K}^0$$

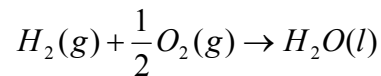
where C_p is a function of temperature. Note that if phase changes occur over the temperature range, the change in entropy of those phase

changes must also be included ($\Delta_{Phase} S_T^0 = \frac{Q_{Phase}}{T_{Phase}} = \frac{nL^0_{Phase}}{T^0_{Phase}}$). Values of \bar{S}_{298K}^o can be found in tables of thermodynamic data.

- Internal energy, Enthalpy, Helmholtz energy, and Gibbs free energy of every *element* in its most stable state of aggregation, at 1 atmosphere and 298.15 K is assigned the value of zero.
- A pure ideal gas, pure liquid and pure solid, exists in standard state at 298K, 1 atmosphere. Dissolved or solute species, including electrolytes, non-electrolytes, and individual ions, are in their standard states if their activities (or effective concentrations) are unity in molar quantities, 298K, 1 atmosphere.

Be advised, Enthalpy, Entropy, and Gibbs free energy of reactions at standard state are based on the **presumption** that the reaction will go to 100% completion. Since all chemical reactions are reversible to some extent, 100% completion is never realized! Real reactions never occur at standard state, however it is the standard state reaction which will provide a basis for the thermodynamics of the non-standard state reaction, discussed later.

3. Standard molar enthalpy of formation. With the standard state reference basis, it is possible to tabulate values for the enthalpy of formation of compounds. Consider the *formation* reaction:



In principle, we perform this reaction under standard state conditions. The reaction is performed in a 1 atmosphere constant pressure vessel. We further extract (or add) heat, *the heat of formation*, to maintain a constant temperature within the vessel. Since the standard enthalpy of the elements in their most stable state are assigned the value of zero, they need not be further considered.

$$\Delta_f \bar{H}_{298K}^0 = \bar{H}_{H_2O(l)}^0 - \left(\bar{H}_{H_2(g)}^0 + \frac{1}{2} \bar{H}_{O_2(g)}^0 \right) = \bar{H}_{H_2O(l)}^0 - 0 = -68.32 \text{ Kcal/mole}$$

Standard enthalpy of formation values are often obtained from calorimetric experiment or C_p data, although once a few key values are determined, many more standard enthalpy of formation values may be computed for other compounds.

The following table is typical of the types of thermo chemical data tabulated in various sources such as the “Handbook of Physics and Chemistry” published by CRC.

Table I. Thermodynamic values for various materials.

Gas		$C_p = A+BT+CT^2$, 300-1500 K, cal/mole K			$\Delta_f G^{\circ}_{298}$ kcal/mole	$\Delta_f H^{\circ}_{298}$ kcal/mole	S°_{298} cal/moleK
		A	B	C			
Hydrogen (g)	H ₂	6.964	-1.960E-04	4.757E-07	0	0	31.211
Nitrogen (g)	N ₂	6.457	1.389E-03	-6.900E-08	0	0	45.767
Oxygen (g)	O ₂	6.117	3.167E-03	-1.005E-06	0	0	49.003
Carbon vapor	C				160.85	171.7	37.76
Carbon monoxide(g)	CO	6.350	1.811E-03	-2.675E-07	-32.8079	-26.4157	47.301
Water (g)	H ₂ O	7.136	2.640E-03	4.590E-08	-54.5657	-57.7979	45.106
Carbon Dioxide(g)	CO ₂	6.339	1.014E-02	-3.415E-06	-94.2598	-94.0518	51.061
Ethane (g)	C ₂ H ₆	2.322	3.804E-02	-1.097E-05	-7.86	-20.236	54.85
Methane (g)	CH ₄	3.204	1.841E-02	-4.480E-06	-12.14	-17.889	44.05
Ethene (g)	C ₂ H ₄	3.019	2.821E-02	-8.537E-06	16.282	12.496	52.45
Ammonia (g)	NH ₃	5.920	8.963E-03	-1.764E-06	-3.976	-11.04	46.01
Air (g)		6.386	1.762E-03	-2.656E-07			

		cal/moleK 293K → 373 K			$\Delta_f G^{\circ}_{298}$ Kcal/mole	$\Delta_f H^{\circ}_{298}$ Kcal/mole	S°_{298} cal/molK
Liquid		A	B	C			
Water(l)	H ₂ O	21.5	-2.29E-2	3.72E-5	-56.7	-68.32	16.716

$$C_p^{\circ} \text{ at } 15.5 \text{ C} = 1.00 \text{ cal/gK} \quad L_f^{\circ} = 79.7 \text{ cal/g at } 0 \text{ C} \quad L_v^{\circ} = 539 \text{ cal/g at } 100 \text{ C}$$

4. Standard Enthalpy change of a Reaction. In a manor similar to finding the enthalpy of formation, the change in enthalpy of a reaction can now be obtained directly from the balanced reaction equation, and the standard molar enthalpies of formation for the reactants and products. The procedure is quite simple in principle, we obtain the enthalpy's of formation for all reactants and products, and subtract the sum of the enthalpy's of the reactants from the sum of the enthalpy's of the products; all being obtained at standard state.

$$\Delta_r H^{\circ} = \sum \Delta_f H^{\circ}(\text{products}) - \sum \Delta_f H^{\circ}(\text{reactants})$$

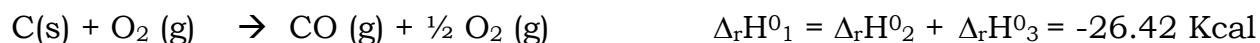
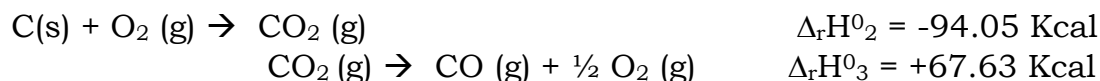
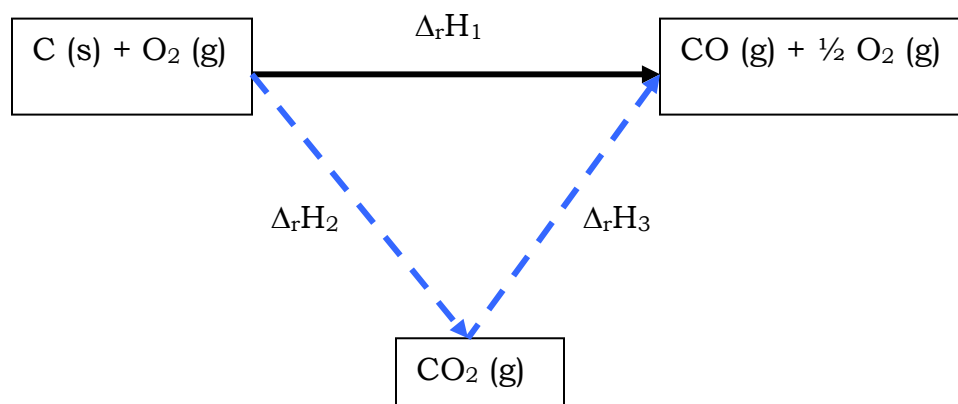
Consider the reaction: $\text{CO (g)} + \frac{1}{2} \text{O}_2 \text{ (g)} \rightarrow \text{CO}_2 \text{ (g)}$

It is desired to obtain the change in enthalpy for this reaction under standard conditions. The procedure starts by acquiring the standard molar enthalpy of formation for all components (1 atm, 298K, in Kcal/mole) from Table I. The calculation is concluded by subtracting the change in enthalpy of formation of the reactants, from that of the products. Notice that since O₂ is in its most stable state at standard conditions, its enthalpy of formation is zero.

$$\begin{aligned} & \{1 \text{ mole CO}_2 \text{ (-94.05 Kcal/mole)} \\ & - (1 \text{mole CO (-26.41 Kcal/mole)} + 1/2 \text{ mole O}_2 \text{ (0 Kcal/mole)} \\ & \Delta_r H^{\circ}_{298} = - 67.64 \text{ Kcal} \end{aligned}$$

Consider the reaction: $\text{C (graphite)} + \text{O}_2 (\text{g}) \rightarrow \text{CO}(\text{g}) + \frac{1}{2} \text{O}_2 (\text{g})$

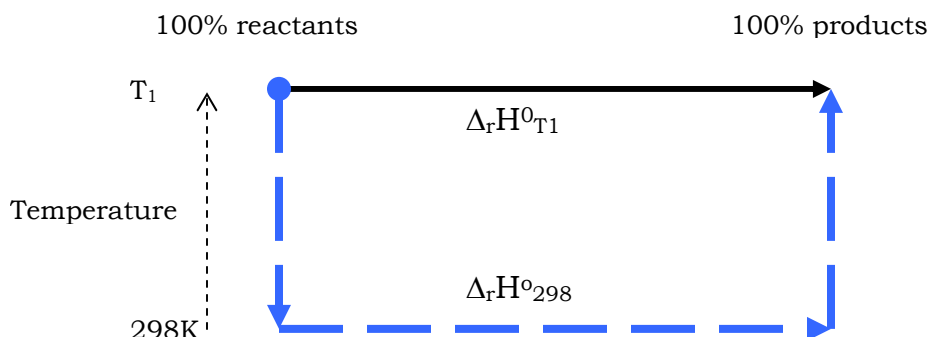
It is desired to obtain the change in enthalpy for this reaction under standard conditions. Due to the strict control of the oxygen required, this reaction is difficult to perform. However, if we recall that enthalpy is a function of state, then the change in enthalpy must be independent of the path of the reaction. Thus, we devise an alternate set of reactions which can be carried out (or for which the reaction enthalpy's are known). For the reactions shown below, $\Delta_r H_1^0 = \Delta_r H_2^0 + \Delta_r H_3^0$. This is **Hess's Law**.



Hess's law may be used with any State function at standard state.

5. Temperature Dependence of the change in Enthalpy of a Reaction.

In general, ΔH will change with temperature. To determine a reaction's change in enthalpy at a temperature other than 298K, we have but to remember that ΔH is a function of state. We exploit this fact by inventing a second reaction path connecting the initial and final states of the reactants and products through the standard temperature as seen in the schematic diagram below.



First, the temperature of the reactants are reduced from T_1 to 298K. Second, the reaction is carried out at standard state (298K). Finally, we elevate the products from 298K to T_1 . The sum of these enthalpies is equivalent to the change in enthalpy for the reaction at T_1 . This is **Kirchhoff's law**; applicable to any state function.

$$\Delta_r H_{T_1}^0 = \int_{T_1}^{298} n C_{p, \text{reac.}} dT + \Delta_r H_{298K}^0 + \int_{298}^{T_1} n C_{p, \text{prod.}} dT$$

If the specific heats, C_p , are not constant over the temperature range, we have little choice but to perform the integrals. To do so requires the availability of C_p as a function of T . Many sources of thermo-chemical data contain these functions.

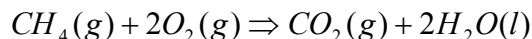
If the temperature range is small enough so that we may consider all C_p 's constant, we may reduce the above equation by swapping the limits of integration on the first integral, and removing the amount and specific heat to give,

$$\Delta_r H_{T_1}^0 = \Delta_r H_{298K}^0 + \Delta_r \hat{C}_p (T - 298)$$

$$\text{where } \Delta_r \hat{C}_p = \sum (n C_p)_{i, \text{Prod.}} - \sum (n C_p)_{j, \text{Reac.}}$$

Example 1. One mole of methane is to be reacted under stoichiometric conditions with air at 298 K, at a constant pressure of 1 atmosphere, in an adiabatic and isobaric container. Determine the enthalpy of combustion, $\Delta_{\text{combustion}} \bar{H}_{298K}^0$, and the final temperature of the products.

We start by writing the balanced reaction for methane and oxygen:



We next look up the standard molar enthalpy of formation for the reactants and products from the Table I.

The standard state change in enthalpy for the reaction is:

$$\Delta_r H^0 = \sum \Delta_f H_{298}^0 (\text{products}) - \sum \Delta_f H_{298}^0 (\text{reactants})$$

$$\begin{aligned} \Delta_r H_{298}^0 &= \{1 \text{ mole}(-94.05 \text{ kcal/mole}) + 2 \text{ mole} (-68.32 \text{ kcal/mole})\} \\ &\quad - \{1 \text{ mole}(-17.89 \text{ kcal/mole}) + 2 \text{ mole} (0 \text{ kcal/mole})\} \end{aligned}$$

$$= \mathbf{-212.8 \text{ kcal/mole of methane}}$$

This value is also the standard molar enthalpy of combustion at 298 K!

To determine the final temperature, we will use Kirchhoff's law. For this example, we need to raise the temperature of the products to T_{final} . This will also include a phase change for water liquid to water vapor. Finally, since air is 77% nitrogen (by weight), we must also include the proper amount of nitrogen and its change in temperature.

We determine the number of moles of N_2 , which accompany the 2 moles of O_2 . Air is a mixture of 23% oxygen and 77% nitrogen by weight (trace gases will not be considered).

Selecting as a basis, 1 gram of air,

$$.23 \text{ grams } O_2 + .77 \text{ grams } N_2 = 1 \text{ gram Air}$$

so in one gram of air, the moles of O_2 and N_2 are

$$.23 \text{ g (1 mole/32 grams)} = .00719 \text{ moles } O_2$$

$$.77 \text{ g (1 mole/28 grams)} = .0275 \text{ moles } N_2$$

and the mole ratio becomes,

$$2 \text{ moles } O_2 \text{ (.0275 moles } N_2 / .00719 \text{ moles } O_2) = 7.65 \text{ moles } N_2$$

2 O_2 : 7.65 N_2

The final steps will consume the enthalpy of combustion to raise the products, and the spectator gas (N_2), to their final temperature. Notice that we must include the enthalpy of vaporization for the liquid water. For ease of calculation, we will compute this transition in two stages: $298K \rightarrow 373K$, and $373K \rightarrow T_{\text{final}}$.

Water: liq @ 298K \rightarrow vapor @ 373K, stage 1:

There are 2 moles, or 36 grams of water. From Table I, $C_{p, \text{liq}} = 1 \text{ cal/g K}$, and $L_v = 539 \text{ cal/g}$.

$$\Delta_{298 \rightarrow 373K} H^0(\text{liq}) = m C_p \Delta T = 36_{\text{grams}} * 1_{\text{cal/gK}} * (373_K - 298_K) = 2700 \text{ cal} = 2.7 \text{ Kcal}$$

$$\Delta_{\text{vap}} H^0 = m * L_v = 36_{\text{grams}} * 539_{\text{cal/gram}} = 19404 \text{ cal} = 19.404 \text{ Kcal}$$

$$\Delta_{298, \text{liq} \rightarrow 373, \text{vap}} H^0 = 2.7 + 19.4 = 22.1 \text{ Kcal}$$

CO_2 : 298K \rightarrow 373K, stage 1:

For the gas phase materials, we will use a curve fit for C_p since there is expected to be a wide range in temperature. From the above table, $C_p = A + B * T + C T^2$ in cal/mole K

Since $\Delta H = Q$ for the constant pressure process,

$$\Delta_{298 \rightarrow 373K} H^0 = n \int_{298}^{373K} C_p dT = n \int_{298}^{373} (A + B T + C T^2) dT = n \left[A T + \frac{1}{2} B T^2 + \frac{1}{3} C T^3 \right]_{298K}^{373K}$$

$$\Delta_{298 \rightarrow 373K} H^0 = 1_{moles} \left\{ 6.339(373 - 298) + \frac{.01014}{2}(373^2 - 298^2) - \frac{.000003415}{3}(373^3 - 298^3) \right\}$$

$$= 701.6 \text{ cal} = .7016 \text{ Kcal}$$

N₂: 298K → 373K, stage 1:

The procedure for CO₂ above is followed.

$$\Delta_{298 \rightarrow 373K} H^0 = 7.65_{moles} \left(6.457(373 - 298) + \frac{.001389}{2}(373^2 - 298^2) - \frac{.000000069}{3}(373^3 - 298^3) \right)$$

$$= 3968 \text{ cal} = 3.968 \text{ Kcal}$$

Stage 1, summary:

22.1Kcal + .7016 Kcal + 3.968 Kcal = **26.77 Kcal** of heat must enter the reaction products to convert the liquid water to vapor and raise their temperature to 373 K. This heat comes from the reaction. Any additional heat (Stage 2) will raise the temperature of the products from 373K, to their final temperature.

$$\Delta_r H^0 + \Delta H_{Stage1}^0 + \Delta H_{Stage2}^0 \equiv 0_{Adiabatic}$$

$$- 212.8_{Kcal} + 26.77_{Kcal} + \Delta H_{Stage2}^0 = 0$$

$$- 186.03_{Kcal} + \Delta H_{Stage2}^0 = 0$$

Stage 2

All components are now in gas phase at 373K. We will use the integral form as was used for the gases in stage 1 to determine the final temperature. Note that a factor of 1000 cal/Kcal will be included to convert from cal, to Kcal.

$$- 186.03 + \frac{2_{moles}}{1000_{cal/Kcal}} \left\{ 7.136(T_f - 373) + \frac{.00264}{2}(T_f^2 - 373^2) + \frac{.0000000459}{3}(T_f^3 - 373^3) \right\}$$

$$+ \frac{1_{mole}}{1000_{cal/Kcal}} \left\{ 6.339(T_f - 373) + \frac{.01014}{2}(T_f^2 - 373^2) - \frac{.000003415}{3}(T_f^3 - 373^3) \right\}$$

$$+ \frac{7.65_{moles}}{1000_{cal/Kcal}} \left\{ 6.457(T_f - 373) + \frac{.001389}{2}(T_f^2 - 373^2) - \frac{.000000069}{3}(T_f^3 - 373^3) \right\} = 0$$

As can be seen, the above equation is cubic in T_f. Our solution will be by trial and error. The above calculation was entered in an Excel spreadsheet, and T_f was adjusted until the equation equaled zero.

$$T_{\text{final}} = 2296 \text{ K}$$

Careful observation of the data in Table I shows that the C_p data is valid for the range: 300K to 1500K. The final temperature, as computed, is beyond that range. We must therefore consider the final temperature as only approximate although the method is sound. An approximate solution could also have been obtained by selecting a representative values of C_p for the range of temperatures expected, and using $Q = nC_p\Delta T$ rather than the integral.

T_{final} as obtained is often called the *Adiabatic Flame Temperature*. This temperature is seldom realized in practice; however it is used as an upper design limit for material selection when constructing a constant pressure reaction vessel.

6. Standard Change In Gibbs Free Energy of a Reaction. In a manor similar to finding the enthalpy change for a reaction, the change in Gibbs Free Energy of a reaction can be obtained directly from the *balanced* reaction equation, and the standard molar Free Energy of formation for the reactants and products. The procedure is quite simple in principle. We obtain the Free Energy's of formation for all reactants and products, then subtract the sum of the Free Energy's of the reactants from the sum of the Free Energy's of the products; all being obtained at standard state.

$$\Delta_r G^0 = \sum \Delta_f G^0(\text{products}) - \sum \Delta_f G^0(\text{reactants})$$

(Note that other methods to compute the change in free energy of a reaction exist and are discussed in the next section.)

Example 2. Determine the change in Gibbs Free Energy for the combustion reaction, $CH_4(g) + 2O_2(g) \Rightarrow CO_2(g) + 2H_2O(l)$, under standard state conditions. Will this reaction proceed spontaneously as written?

From Table I, the formation Gibbs free energy values are collected.

For the products:

$$(1 \text{ mole } CO_2 \text{ gas}) * (-94.2598 \text{ Kcal/mole}) + (2 \text{ moles } H_2O \text{ liq}) * (-56.7 \text{ Kcal/mole}) \\ = -207.7 \text{ Kcal}$$

For the reactants:

$$(1 \text{ mole } CH_4 \text{ gas}) * (-12.14 \text{ Kcal/mole}) + (2 \text{ mole } O_2 \text{ gas}) * (0.0 \text{ Kcal/mole}) \\ = -12.14 \text{ Kcal}$$

$$\Delta_r G_{298K}^0 = [-207.7] - [-12.14] = \mathbf{-195.6 \text{ Kcal}}$$

Since the change in Gibbs Free Energy is less than zero, this reaction should be able to proceed spontaneously under standard state conditions.

7. Temperature Dependence of Gibbs Energy change of a Reaction. In the consideration of how the Gibbs free energy of a reaction varies with temperature (pressure remaining constant), we recall that the Gibbs energy can be expressed in terms of enthalpy and entropy as follows:

$$\Delta G \equiv \Delta H - \Delta(TS)$$

Applying the above to a reaction at standard state conditions gives:

$$\Delta_r G_{298}^0 = \Delta_r H_{298}^0 - (298)\Delta_r S_{298}^0$$

To determine the change in Gibbs free energy of a reaction at a temperature other than 298, we recall that both the enthalpy change and entropy change of the reaction are functions of temperature. Our method is simply adjust these quantities for a new temperature and utilize the above equation.

The basic principle for our temperature adjustment lies in Kirchoff's Law, although the details depend on whether we can consider the specific heats' of the reactants and products constant over the temperature range $298\text{K} \rightarrow T$, and whether any of the materials undergo a phase transformation over that temperature range. Section 1 of this chapter describes the method to adjust the entropy to a new temperature, and section 5 describes the similar adjustment for the enthalpy. The adjustments are (assuming no phase transformations):

$$\Delta_r H_{298\text{K} \rightarrow T}^0 = \int_{298}^T \sum (nC_p)_{i, \text{Prod}} dT - \int_{298}^T \sum (nC_p)_{j, \text{Reac}} dT$$

or if the specific heat values may be considered constant,

$$\Delta_r H_{298 \rightarrow T}^0 = \Delta_r \hat{C}_p (T - 298) ,$$

$$\text{where } \Delta_r \hat{C}_p = \sum (nC_p)_{i, \text{Prod}} - \sum (nC_p)_{j, \text{Reac}} .$$

and,

$$\Delta_r S_{298\text{K} \rightarrow T}^0 = \int_{298}^T \sum \left(\frac{nC_p}{T} \right)_{i, \text{Prod}} dT - \int_{298}^T \sum \left(\frac{nC_p}{T} \right)_{j, \text{Reac}} dT$$

or, for constant specific heat,

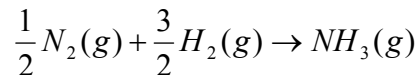
$$\Delta_r S_{298 \rightarrow T}^0 = \Delta_r \hat{C}_p \ln \left(\frac{T}{298} \right)$$

The change in Gibbs free energy for the reaction at the new temperature, standard pressure is then,

$$\Delta_r G_T^0 = \left(\Delta_r H_{298}^0 + \Delta_r H_{298\text{K} \rightarrow T}^0 \right) - T \left(\Delta_r S_{298}^0 + \Delta_r S_{298\text{K} \rightarrow T}^0 \right)$$

Example 3. For the reaction to produce Ammonia gas from elemental Hydrogen and Nitrogen, determine the change in Gibbs free energy for the reaction at both 298K and at 500K, 1 atmosphere. How does the Gibbs free energy change with temperature? Use specific heat values at 400K and assume the specific heat may be considered constant over the specified temperature range?

We write the balanced reaction:



and collect the required information from Table I:

	$\Delta_f G_{298}^0$ Kcal/mole	$\Delta_f H_{298}^0$ Kcal/mole	S_{298}^0 cal/K/mole	$C_{p,400K}$ cal/K/mole
NH ₃ (g)	-3.976	-11.04	46.01	9.22
N ₂ (g)	0	0	45.8	7.00
H ₂ (g)	0	0	31.2	6.96

Next, the reaction free energy, enthalpy, and entropy changes are computed at standard state.

$$\Delta_r H_{298}^0 = (1 \text{ mole NH}_3)(-11.04 \text{ Kcal/mole}) - (\frac{1}{2} \text{ mole N}_2)(0 \text{ Kcal/mole}) - (\frac{3}{2} \text{ mole H}_2)(0 \text{ kcal/mole}) = \mathbf{-11.04 \text{ Kcal}}$$

$$\Delta_r S_{298}^0 = (1 \text{ mole NH}_3)(46.01 \text{ cal/K/mole}) - (\frac{1}{2} \text{ mole N}_2)(45.8 \text{ cal/K/mole}) - (\frac{3}{2} \text{ mole H}_2)(31.2 \text{ cal/K/mole}) = \mathbf{-23.69 \text{ cal/K}}$$

$$\Delta_r G_{298}^0 = (1 \text{ mole NH}_3)(-3.976 \text{ Kcal/mole}) - (\frac{1}{2} \text{ mole N}_2)(0 \text{ Kcal/mole}) - (\frac{3}{2} \text{ mole H}_2)(0 \text{ kcal/mole}) = \mathbf{-3.976 \text{ Kcal}}$$

We verify the change in Gibbs free energy for the reaction using the equation, $\Delta_r G_{298}^0 = \Delta_r H_{298}^0 - T \Delta_r S_{298}^0 = -11.04 \text{ Kcal} - 298\text{K} (-.02369 \text{ Kcal/K}) = -3.976 \text{ Kcal} !$

Since the specific heat values will be considered constant, we compute the change in heat capacity, nC_p , for the reaction:

$$\Delta_r \hat{C}_p = (1 \text{ mole NH}_3)(9.22 \text{ cal/K/mole}) - (\frac{1}{2} \text{ mole N}_2)(7.00 \text{ cal/K/mole}) - (\frac{3}{2} \text{ mole H}_2)(6.96 \text{ cal/K/mole}) = \mathbf{-4.72 \text{ cal/K}}$$

Finally, we assemble the equation for the change in Gibbs free energy at the new temperature:

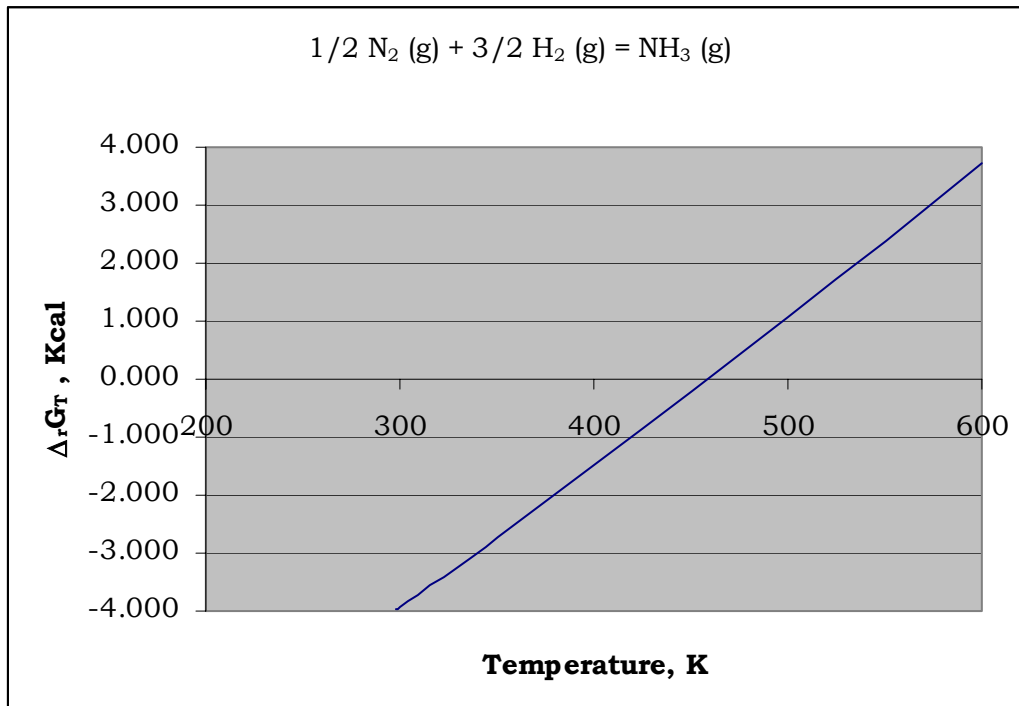
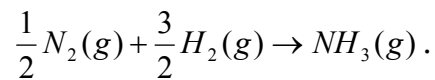
$$\Delta_r G_T^0 = (\Delta_r H_{298}^0 + \Delta_r H_{298K \rightarrow T}^0) - T(\Delta_r S_{298}^0 + \Delta_r S_{298K \rightarrow T}^0)$$

$$\Delta_r G_T^0 = (\Delta_r H_{298}^0 + \Delta_r \hat{C}_p (T - 298)) - T \left(\Delta_r S_{298}^0 + \Delta_r \hat{C}_p \ln \left(\frac{T}{298} \right) \right)$$

and evaluate it at 500K.

$$\Delta_r G_{500K}^0 = \left(-11.04 - \frac{4.72}{1000} (500 - 298) \right) - 500 \left(\frac{-23.69}{1000} + \frac{-4.72}{1000} \ln \left(\frac{500}{298} \right) \right) = +1.076 \text{ Kcal}$$

Below is a plot of $\Delta_r G_T^0$ as a function of temperature for the reaction:



Notice that $\Delta_r G_T^0$ is positive for temperature values in excess of approximately 460K.

8. Pressure Dependence of Gibbs Energy. The pressure dependence of Gibbs free energy of a pure substance (mixtures are discussed in section 10.), under the constraint of constant temperature, may be obtained in the general case from the below equation,

$$\Delta G \equiv \Delta U + \Delta(PV) - \Delta(TS) = -\int SdT + \int VdP$$

for which $dT = 0$. The result, applicable for constant temperature, is,

$$\int dG = \int VdP$$

Further refinement of the above result will usually require knowledge of how a materials' volume depends on pressure.

Sources of thermo-chemical data often tabulate functions for the isothermal compressibility for various materials. For phase transformations from liquid to vapor, the molar volume of the liquid may often be considered as insignificant. For ideal gases, the ideal gas law may be used as a substitution for volume although one must consider the possibility that the real gas may not behave as ideal at higher pressures and some correction factor will need to be incorporated.

For an ideal gas, $V = \frac{nRT}{P}$ and on substitution,

$$\int_{G_1}^{G_2} dG = nRT \int_{P_1}^{P_2} \frac{1}{P} dP$$

$$G_2 - G_1 = nRT \ln\left(\frac{P_2}{P_1}\right)$$

The above result will be used in section 10. to follow.

9. Chemical Reactions. A chemical reaction is thought to start, in a macroscopic sense, when the reactants are mixed. The actual reaction however requires a process, during which force bonds between atoms are broken, and or formed, or both. In a microscopic sense, the forward rate of the chemical reaction depends on the number of collisions between the reactants per unit of time, and the fraction of those collisions which (due to energy, molecular orientation, and a number of other factors) are actually fruitful in producing a product.

Once any product has been formed, a new reaction is started; the *reverse reaction*. This reverse reaction also has a rate of reaction which is governed by exactly the same principles discussed in the previous paragraph. At the onset of

the reaction, the rate of the forward reaction (due to high concentration) is greater than the rate of the reverse reaction (low concentration) and reaction proceeds in the forward direction. As more product is formed, and more reactant is consumed, the forward reaction rate is reduced and the reverse reaction rate is increased. The reaction reaches a state of chemical equilibrium when both the forward and reverse reaction rates are identical. It must be understood that the forward and reverse reactions do not stop when equilibrium is achieved, they continue to proceed in both directions – at the same rate. The equilibrium is thus a reversible *dynamic* equilibrium. All chemical reactions are reversible to some extent.

When all other conditions are held constant, the rate of the reaction should be expressible as some function of concentration; the big question being what is this function?

To answer this question, consider a reaction for which the reactants and products are mixtures of perfectly ideal gases. By definition, the volume containing these gases is very large when compared to the volume of the gas molecules themselves. There are no internal forces acting between these gas molecules. The gas molecules behave as tiny mechanical particles, each far removed from the other, only effected by collisions with their container, and an occasional collision with another reacting molecule. Under these conditions, **Dalton's law** of partial pressures for a mixture of ideal gases states that each gas component in a mixture of gases acts as if it is independent of the other gases present; each gas component exerting a *partial pressure* on the container. For the component i , $P_i = \frac{n_i}{V} RT$. The concentration of each component is directly proportional to the partial pressure of that component. It is exactly the perfectly ideal nature of the gases that causes Dalton's law to be true. Under ideal conditions, the partial pressure (or actual concentration for the case of a dilute solution) is proportional to the reaction rate.

With a mixture of real gases, intermolecular forces do exist. These forces act to change the effective number of particles, and thus the effective concentrations of the gases involved. This “non-ideal” condition is further exacerbated when the size of the molecule is significant when compared to the container size, when the gases are of high concentration, and when the molecules are of high polarity to list only a few situations. With non-ideal gases (or solutions), the partial pressure (or actual concentration) is a poor measure of the reaction rate. It is the “*effective concentration*”, or **activity** which is proportional to the reaction rate.

In previous sections, the thermodynamics of the “Standard State Reaction” were presented. Recall that the standard state reaction is presumed to go to 100% completion; to have NO reverse reaction! Was our time wasted on the

standard state reaction? No. We have but to “*adjust*” the standard state thermodynamics to the actual chemical activities’ of the reactants and products.

10. Change in Gibbs Free Energy for the General Reaction. We are now ready to extend the results of section 8 to the general reaction. Dalton’s law of partial pressures for a mixture of ideal gases states that each gas component in a mixture of gases acts as if it is independent of the other gases present; each gas exerting a *partial pressure* on the container. The sum of these partial pressures equaling the total pressure on the container. Thus, for n_i moles of the gas component “i”, we revisit the derivation of section 8, recalling that the temperature is held constant.

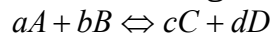
$$\int dG = \int VdP \text{ , where we substitute } V = \frac{n_i RT}{P_i} \text{ for the } i^{\text{th}} \text{ component,}$$

$$n_i \int_{\bar{G}_i^0}^{\bar{G}_i} d\bar{G} = n_i RT \int_{1 \text{ atm}}^P \frac{1}{P_i} dP$$

$$n_i(\bar{G}_i - \bar{G}_i^0) = n_i RT \ln\left(\frac{P_i}{1 \text{ atm}}\right)$$

$$n_i(\bar{G}_i - \bar{G}_i^0) = n_i RT \ln P_i$$

Next, consider the following reaction of ideal gases:



If carried out under standard state conditions, the change in Gibbs free energy for the reaction is:

$$\Delta_r G^0 = c(\Delta_f \bar{G}_C^0) + d(\Delta_f \bar{G}_D^0) - a(\Delta_f \bar{G}_A^0) - b(\Delta_f \bar{G}_B^0)$$

If however, the reaction is carried out under non-standard state conditions, we arrive at:

$$\Delta_r G = c(\Delta_f \bar{G}_C) + d(\Delta_f \bar{G}_D) - a(\Delta_f \bar{G}_A) - b(\Delta_f \bar{G}_B)$$

When we subtract one equation from the other, and rearrange, we arrive at:

$$\Delta_r G - \Delta_r G^0 = c(\Delta_f \bar{G}_C - \Delta_f \bar{G}_C^0) + d(\Delta_f \bar{G}_D - \Delta_f \bar{G}_D^0) - a(\Delta_f \bar{G}_A - \Delta_f \bar{G}_A^0) - b(\Delta_f \bar{G}_B - \Delta_f \bar{G}_B^0)$$

and can identify each of the four terms on the right as of the form,

$n_i(\bar{G}_i - \bar{G}_i^0) = n_i RT \ln P_i$, previously found. On substitution and rearrangement, we arrive at:

$$\Delta_r G - \Delta_r G^0 = cRT \ln P_C + dRT \ln P_D - aRT \ln P_A - bRT \ln P_B$$

$$\Delta_r G_T = \Delta_r G_T^0 + RT \ln \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right)$$

where the partial pressures must be in atmosphere units, and the exponents in moles. Thus, we have derived the change in Gibbs Free Energy at non-standard state for a reaction involving a mixture of ideal gases.

11. Chemical Equilibrium of a Reaction. As discussed in the Introduction of this chapter (and in detail in chapter I. Thermo-Physics, section 16.3), a chemical system will be in equilibrium when it has no available energy (or what is often called *FREE* energy) to do work. Under constant temperature and pressure conditions, the Gibbs Free Energy state function is interpreted as the available energy ($\Delta G = -\text{Work}_{\text{net}}$) and as such, will predict chemical equilibrium. When $\Delta G < 0$ for the reaction, the reaction can do net work and should proceed spontaneously as written. When $\Delta G = 0$, the reaction can do no net work and is therefore in equilibrium. Thus, at equilibrium,

$$0 = \Delta_r G_T^0 + RT \ln \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right)$$

$$\Delta_r G_T^0 = -RT \ln \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right)$$

The quantity contained in the logarithm will be named the *Equilibrium constant* and is assigned the variable, $K_P = \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right)$.

$$\Delta_r G_T^0 = -RT \ln K_P$$

$$K_P = e^{-\left(\frac{\Delta_r G_T^0}{RT} \right)}$$

The equilibrium constant, K , is often introduced to students by means of kinetic (reaction rate) arguments. Here, we have presented a purely thermodynamic argument. Both are valid and instructive. Notice that the value of the equilibrium constant is a function of temperature, but is NOT a function of concentration since ΔG^0 (unlike ΔG) is based on the Gibbs free energies of the products and reactants *in their standard states*.

When a reaction is not at equilibrium, it is customary to write the Gibbs free energy relationship of section 10. as:

$$\Delta_r G_T = \Delta_r G_T^0 + RT \ln Q_p$$

where Q , the reaction quotient, has the form of the equilibrium constant K . Remember however that Q is based on the actual concentrations of the products and reactants; NOT on their standard states.

12. K, K, and more Ks'. In the area of chemistry, it would seem that the founding fathers had a rather special place in their hearts for the letter **K** (as does this author). A great many constants traditionally are assigned to the letter **K** with a subscript attached to sort out one from the next. In this section, we look at K_P , K_x , K_C , and K_{activity} and the relationship between these **K**'s. What all have in common, is to express the chemical activity of the products and reactants in some reasonable and convenient form. (The **K** values to follow may also be replaced with Q if the reaction is not in equilibrium.)

Partial pressure. As was previously shown, the partial pressures are useful when the reaction involves all gas components, $K_P = \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right)$, at least from a mathematical point of view. However, in practical calculations involving gas-phase systems, it is often more convenient to express quantities of gases in units other than atmospheres of pressure.

Mole fraction. The mole fraction for a component, is the ratio of the number of moles of that component, to the total number of moles of material (both product and reactant) in the reaction, $x_i \equiv \frac{n_i}{n_{\text{total}}} = \frac{P_i}{P_{\text{total}}}$. For an ideal gas, this is also equal to the ratio of the partial pressure of a component to the total pressure. Solving for the partial pressure, $P_i = x_i P$, we replace each partial pressure in K_P as follows:

$$K_P = \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right) = \left(\frac{(X_C P)^c (X_D P)^d}{(X_A P)^a (X_B P)^b} \right) = \left(\frac{X_C^c X_D^d}{X_A^a X_B^b} \right) P^{c+d-a-b} = K_X P^{c+d-a-b}, \text{ where } K_X = \left(\frac{X_C^c X_D^d}{X_A^a X_B^b} \right).$$

K_X is often easier to compute than K_P and can also be used for solutions which behave as ideal.

Concentration. The concentration of a component, is the ratio of the number of moles of that component, to the total number of liters of volume available to be occupied (both product and reactant) in the reaction. The square braces, $[A]$, around the component is short hand for the concentration of that component. For an ideal gas, $P_i = \left[\frac{n_i}{V} \right] RT$. We replace each partial pressure in K_P as follows:

$$K_p = \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right) = \left(\frac{([C]RT)^c ([D]RT)^d}{([A]RT)^a ([B]RT)^b} \right) = \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right) (RT)^{c+d-a-b} = K_C (RT)^{c+d-a-b}$$

, where $K_C = \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$

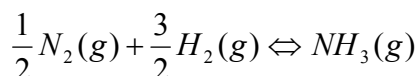
K_C is most useful for solutions which behave as ideal.

Activity. When a chemical system deviates from ideal, the chemical activity of each component must be used. The chemical activity of a component, is proportional to the component's concentration. $a_i = \text{activity} = f_i [C_i]$, where the proportionality "constant" is called the activity coefficient, f . We may replace the concentrations in K_C as follows:

$$K_C = \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right) = \left(\frac{\left(\frac{a_C}{f_C} \right)^c \left(\frac{a_D}{f_D} \right)^d}{\left(\frac{a_A}{f_A} \right)^a \left(\frac{a_B}{f_B} \right)^b} \right) = \left(\frac{a_C^c a_D^d}{a_A^a a_B^b} \right) \frac{K_{\text{activity}}}{\left(\frac{f_C^c f_D^d}{f_A^a f_B^b} \right)}, \text{ where } K_{\text{activity}} = \left(\frac{a_C^c a_D^d}{a_A^a a_B^b} \right)$$

Chemical activities, and activity coefficients are tabled in various chemical data handbooks.

Example 4. Once again consider the reaction:



for which we start with $\frac{1}{2}$ mole of $N_2(g)$ and $\frac{3}{2}$ mole of $H_2(g)$ combined in a 1 atmosphere constant pressure container held at 298K.

Let " f " ($0 \leq f \leq 1$) equal the fraction of completion for this reaction. We seek to determine how the value of the change in Gibbs free energy for this reaction depends on " f ". We assume the gases to behave ideal.

We start by computing the number of moles of each component and the total number of moles at any stage in the reaction.

$$\begin{aligned} NH_3(g): & 1 \text{ mole} * f \\ N_2(g): & \frac{1}{2} \text{ mole} * (1-f) \\ H_2(g): & \frac{3}{2} \text{ mole} * (1-f) \\ \text{Total moles} & = f + \frac{1}{2} * (1-f) + \frac{3}{2} * (1-f) = (2-f) \text{ moles.} \end{aligned}$$

Next, the mole fractions for each component are computed.

$$X_{NH_3} = \frac{f}{(2-f)} \quad X_{N_2} = \frac{1/2(1-f)}{(2-f)} \quad X_{H_2} = \frac{3/2(1-f)}{(2-f)}$$

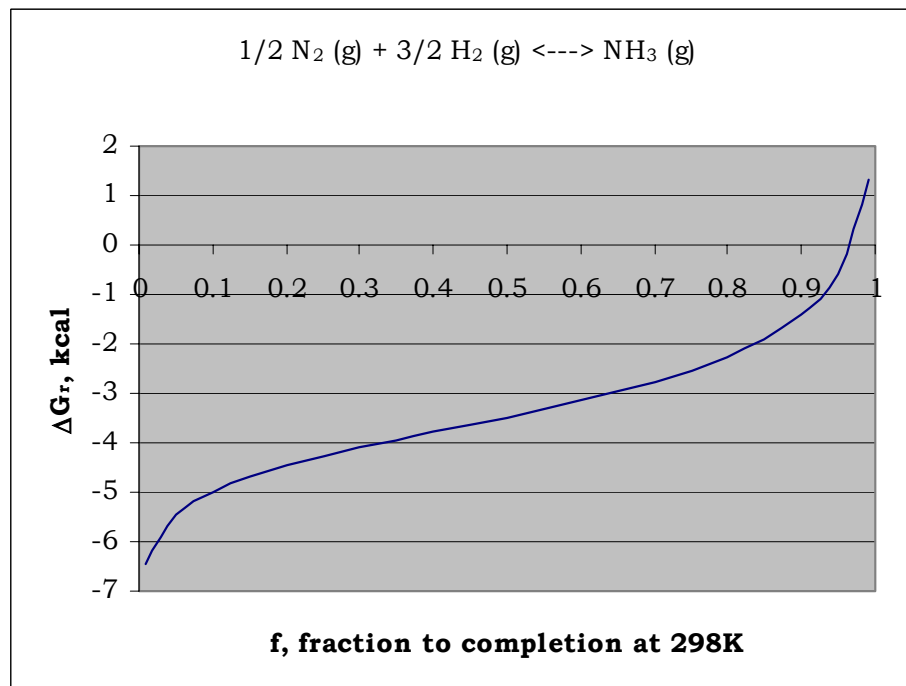
Q_p is now computed using $Q_p = Q_x P^{(1-1/2-3/2)}$. Note that for a pressure of 1 atmosphere, $Q_p = Q_x$.

$$Q_p = \frac{\frac{f}{(2-f)}}{\left(\frac{.5(1-f)}{(2-f)}\right)^5 \left(\frac{1.5(1-f)}{(2-f)}\right)^{1.5}} P^{\left(1-\frac{1}{2}-\frac{3}{2}\right)}$$

and finally, using $\Delta_r G_T = \Delta_r G_T^0 + RT \ln Q_p$, the change in Gibbs free energy for the reaction becomes:

$$\Delta_r G_{298} = -3.976_{Kcal} + (1.986_{cal/moldK}) \left(\frac{1_{Kcal}}{1000_{cal}} \right) 298_K (mole) \ln[Q_p]$$

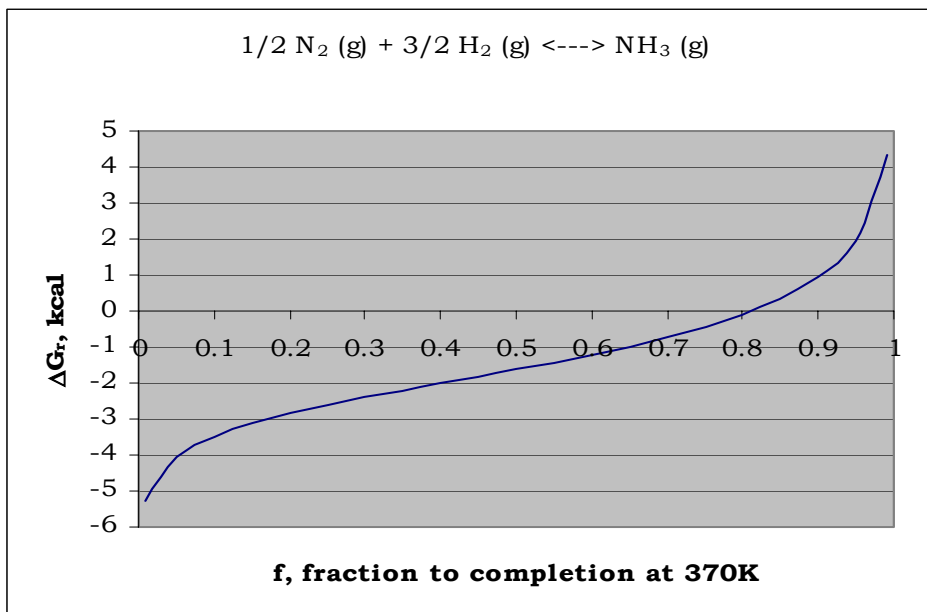
The above function is graphed using Excel to give:



The above graph indicates that when $f=0.97$, $\Delta_r G = 0$. Thus the reaction is predicted to go to 97% completion.

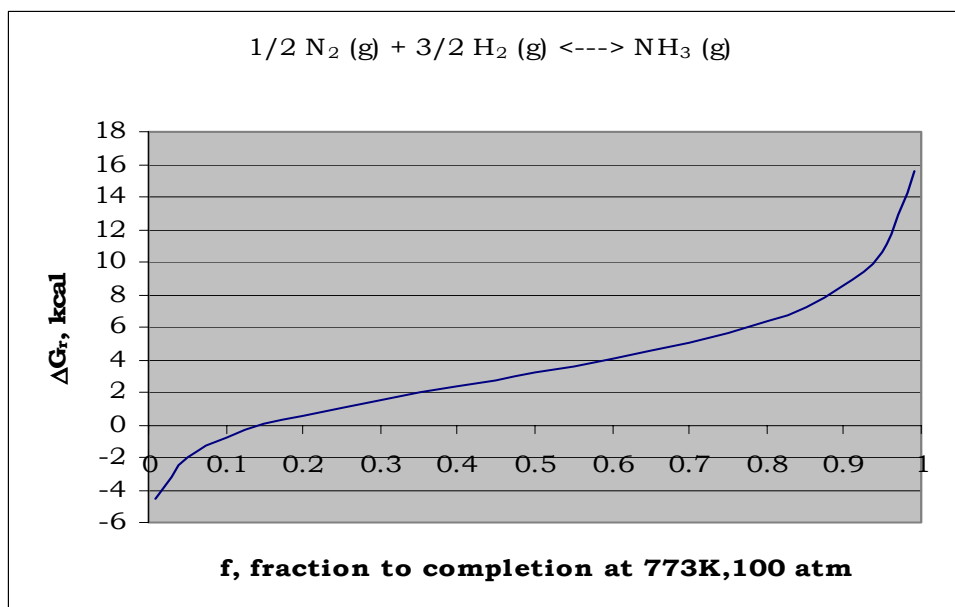
As a technical note, the reaction kinetics at 298 K, 1 atm are very very slow. For this reason, the reaction is not feasible in a practical sense.

The change in Gibbs free energy for the reaction at a temperature of 370K (1 atm) is also computed (adjusting all terms for the new specific heat values at this temperature), and graphed below as a function of reaction completion, f.



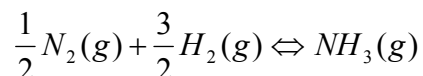
At this elevated temperature, $\Delta_r G = 0$ when the completion is approximately 80%.

Finally, the change in Gibbs free energy for the reaction at a temperature of 773K, 100 atm, is computed (adjusting all terms for the new specific heat values at this temperature, and the new pressure), and graphed below as a function of reaction completion, f.

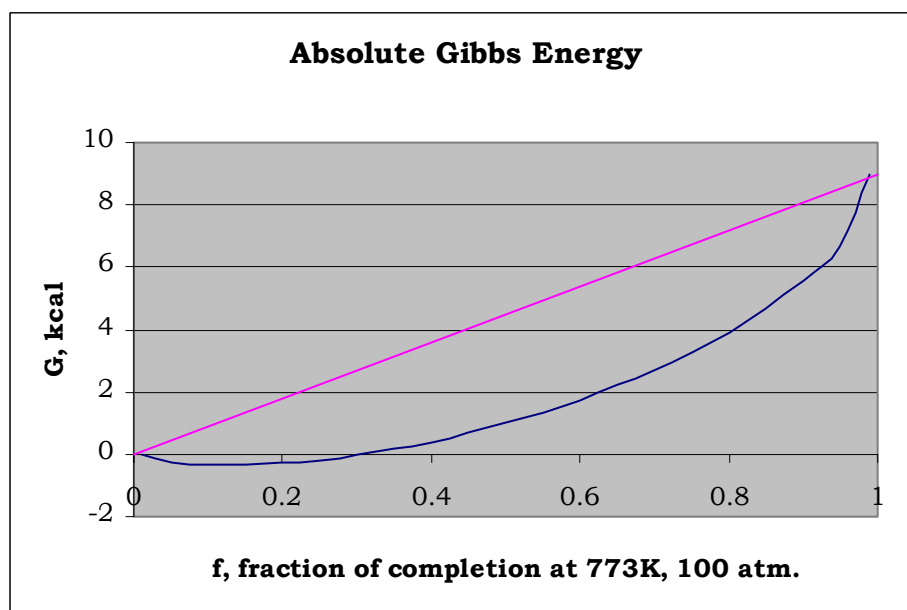


At 773K, 100 atmospheres, $\Delta_r G = 0$ at a completion of approximately 15%. At the elevated temperature and pressure, the kinetics (reaction rate) are much more favorable for the production of ammonia. However, under batch processing, the fraction to completion is very low and would be considered inefficient. If produced by continuous processing however, the yield efficiency is sufficient and economical.

13. Review of Gibbs Free Energy. Below, we have computed the absolute Gibbs Free Energy, G_r , for the reaction:

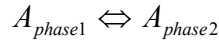


by numeric integration of the previous graph (773K, 100 atm). The values of G_r on the vertical axis are based on the **arbitrary** assignment that the Gibbs Free energy of the pure reactants equal zero. The result of this numeric integration is the curve seen below. The slope of this curve is $\Delta_r G_{773K}^{100atm}$ for the reaction. Note that at $f=.15$ (15%) completion, the slope is zero! This is the completion fraction at equilibrium. It can be seen that for values of $f < .15$, the slope of the curve is negative, indicating a spontaneous reaction at these concentrations. Above 15%, the slope is positive indicating that the reaction is spontaneous in the *opposite* direction (right to left) as written.



Also shown in the graph is a line connecting the point $(f=0, G=0)$ to the point $(f=1, G=+8.94\text{kcal})$. For this reaction, $\Delta_r G_{773K}^0 = +8.94$ kcal, which is the slope of this line. Considering only $\Delta_r G_{773K}^0$ which is greater than zero, we may be tempted to (wrongly) conclude that the reaction is not spontaneous as written at 773K.

14. Phase Equilibrium Transformation Temperature. Suppose we have a pure substance, **A**, existing in two phases (phase 1 and phase 2) that are in equilibrium with each other, such as solid and liquid or liquid and vapor.



Since the two phases are in equilibrium, the change in molar free energy $\Delta_f \bar{G}$ must be zero. This implies that at equilibrium, the molar free energy of phase 1 must be equal to the molar free energy of phase 2. Further, if some small change in the molar free energy of phase 1 were to take place, an identical change in the molar free energy of phase 2 must take place to maintain the equilibrium.

$$\begin{aligned}\bar{G}_{\text{phase1}} &= \bar{G}_{\text{phase2}} \\ d\bar{G}_{\text{phase1}} &= d\bar{G}_{\text{phase2}}\end{aligned}$$

We set out to determine the temperature at which an equilibrium phase transformation will occur, at a standard pressure of one atmosphere. From Section 6. we recall (for 1 mole of material),

$$\Delta_f \bar{G}_T^0 = \Delta_f \bar{G}_T^0(\text{phase2}) - \Delta_f \bar{G}_T^0(\text{phase1})$$

and at equilibrium, the reaction free energy must equal zero. Thus,

$$\Delta_f \bar{G}_T^0(\text{phase1}) = \Delta_f \bar{G}_T^0(\text{phase2})$$

We now employ the results of Section 7. to each of the formation free energy's above.

$$\left(\left(\Delta_f \bar{H}_{298}^0 + \Delta \bar{H}_{298 \rightarrow T}^0 \right) - T \left(\Delta_f \bar{S}_{298}^0 + \Delta \bar{S}_{298 \rightarrow T}^0 \right) \right)_{\text{phase1}} = \left(\left(\Delta_f \bar{H}_{298}^0 + \Delta \bar{H}_{298 \rightarrow T}^0 \right) - T \left(\Delta_f \bar{S}_{298}^0 + \Delta \bar{S}_{298 \rightarrow T}^0 \right) \right)_{\text{phase2}}$$

(since the mathematical treatment of phase 1 will be identical to phase 2, we save some space)

We now replace the temperature dependent values above with the appropriate integrals.

$$\Delta_f \bar{G}_T^0(\text{phase 1}) = \left(\Delta_f \bar{H}_{298}^0 + 1 \text{mole} \int_{298}^T C_P dT \right) - T \left(\Delta_f \bar{S}_{298}^0 + 1 \text{mole} \int_{298}^T \frac{C_P}{T} dT \right) = \Delta_f \bar{G}_T^0(\text{phase 2})$$

As can be seen, once we replace C_P with its appropriate function of temperature, and perform the required integrations, solving the result for temperature will be next to impossible. Thus, we will employ a different (and informative) tactic; we will replace C_P and perform the integrations for both phase 1 and phase 2. Then we will plot the resulting $\Delta_f \bar{G}_T^0$ for each phase as a function of temperature. It is expected that these two curves will intersect, and the intersection temperature will be the equilibrium phase transformation temperature.

Example 5.

We select the material H_2O , and the transformation from liquid to vapor. The necessary data is found in Table I. The goal is to determine the equilibrium liquid to vapor phase transition temperature. The approach is outlined above.

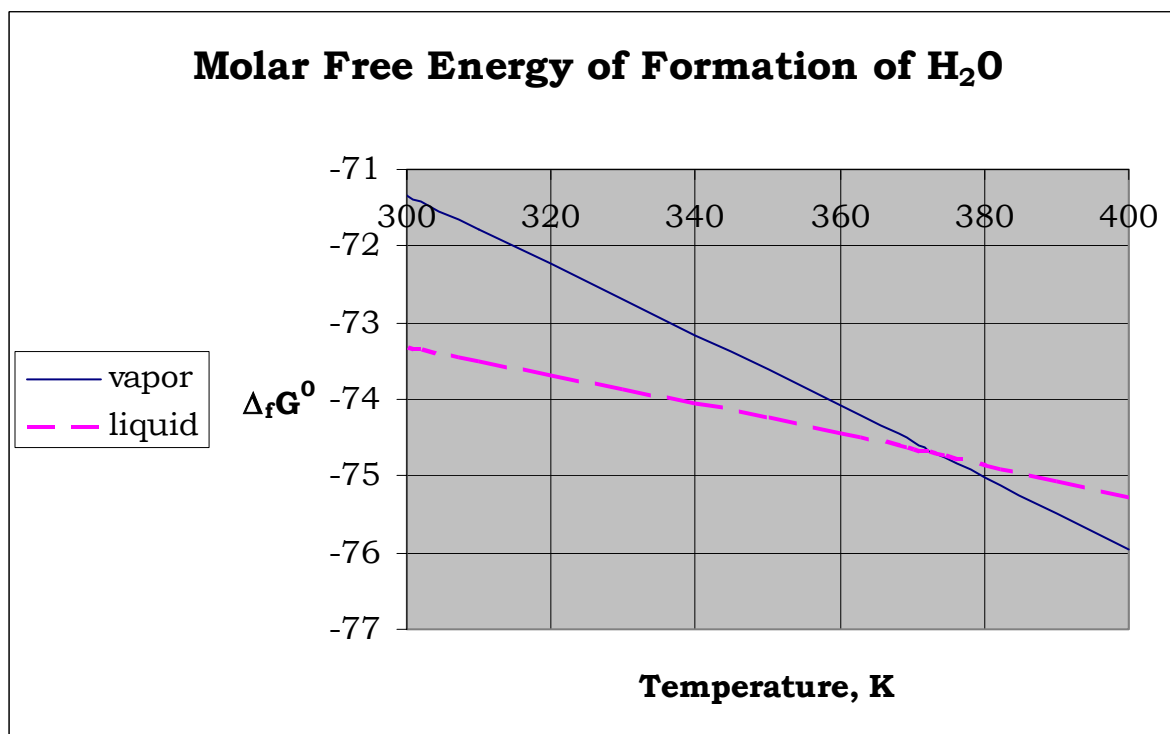
The results of the C_P substitution and integration is,

$$\Delta_f \bar{G}_T^0 = \Delta_f \bar{H}_{298}^0 + \left\{ A(T - 298) + \frac{B}{2}(T^2 - 298^2) + \frac{C}{3}(T^3 - 298^3) \right\} \frac{1 \text{ kcal}}{1000 \text{ cal}}$$

$$- T \left(\Delta_f \bar{S}_{298}^0 + A \ln \left(\frac{T}{298} \right) + B(T - 298) + \frac{C}{2}(T^2 - 298^2) \right) \frac{1 \text{ kcal}}{1000 \text{ cal}}$$

The factor of 1/1000 is required because A, B, C, S from Table I. are in calories. The result of the computation will be in Kcal.

We show the results of our computations in the graph below.



Below 373K, it is seen that the Free Energy of the liquid is more negative than that of the vapor. Thus, liquid is the favored phase at these temperatures. Above 373K, vapor is the favored phase since the free energy of that phase is more negative. At 373K, both liquid and vapor phases have the same free energy per mole, thus their difference is zero; since $\Delta_r \bar{G}_T^0 = 0$, The phase reaction is in equilibrium.

Although we have successfully predicted the equilibrium temperature, one must remember that the outcome is only as good as the data used. Measurement of C_P as a function of temperature is a tedious exercise, and the subsequent curve fit will contain some error; often too much. The direct measurement of the transformation temperature is far easier and accurate.

15. Variation of Phase Equilibrium Temperature with Pressure. Review the first two paragraphs of Section 13. We have shown that for the transformation, $A_{phase1} \Leftrightarrow A_{phase2}$, that the molar free energy relationships at equilibrium must be:

$$\begin{aligned}\bar{G}_{phase1} &= \bar{G}_{phase2} \\ d\bar{G}_{phase1} &= d\bar{G}_{phase2}\end{aligned}$$

Recalling that $dG = V dP - S dT$, we replace the differentials in the above as follows:

$$\begin{aligned}d\bar{G}_{phase1} &= d\bar{G}_{phase2} \\ \bar{V}_1 dP - \bar{S}_1 dT &= \bar{V}_2 dP - \bar{S}_2 dT \\ (\bar{S}_2 - \bar{S}_1) dT &= (\bar{V}_2 - \bar{V}_1) dP \\ \Delta\bar{S} dT &= \Delta\bar{V} dP\end{aligned}$$

For an equilibrium phase transformation at constant pressure, the change in entropy change is $\Delta_{phase}\bar{S} = \frac{\Delta_{phase}\bar{H}}{T_{phase}}$ and on substitution gives,

$$\frac{\Delta_{phase}\bar{H}}{T_{phase}} dT = \Delta_{phase}\bar{V} dP$$

This is the *Clapeyron* equation. One of its many uses is to describe how the equilibrium phase transformation temperature is effected by pressure. An alternate form of the equation is:

$$\frac{dT}{dP} = T \frac{\Delta\bar{V}}{\Delta\bar{H}}$$

Example 6. How does the equilibrium freezing temperature of pure water change with pressure?

Our reaction is: $H_2O(sol) \rightarrow H_2O(liq)$

The above result will be used to solve this problem. First, the required data is collected (from the Handbook of chemistry and physics, CRC).

Density of ice at 0C = .917 gr/ml
 Density of water at 0C = .9999 gr/ml
 molecular weight of H₂O = 18 gr/mole

The molar volume of each is now computed,

For Ice, $\frac{1ml}{.917gr} \frac{18gr}{1mole} \frac{1liter}{1000ml} = .0196 \text{ liter/mole}$

For water, $\frac{1ml}{.9999gr} \frac{18gr}{1mole} \frac{1liter}{1000ml} = .0180 \text{ liter/mole}$

The change in molar volume is,

$$\Delta \bar{V} = \bar{V}_{liq} - \bar{V}_{solid} = .0180 \text{ liter/mole} - .0196 \text{ liter/mole} = \mathbf{-.00160 \text{ liter/mole}}$$

From Table I., $L_f = 79.7 \text{ cal/gram}$. Thus,

$$\Delta_{sol \rightarrow liq} \bar{H} = \frac{79.7 \text{ cal}}{\text{gr}} \frac{18 \text{ gr}}{\text{mole}} \frac{.08205 \text{ liter atm}}{1.986 \text{ cal}} = \mathbf{59.3 \text{ liter atm/mole}}$$

Finally, we compute $\frac{dT}{dP} = T \frac{\Delta \bar{V}}{\Delta \bar{H}} = 273.15 \text{ K} \frac{-.00160 \text{ liter/mole}}{59.3 \text{ liter atm/mole}} = \mathbf{-.00737 \text{ K/atm}}$

We have computed the change in the equilibrium freezing temperature with pressure for water. Note that this value is only accurate in the vicinity of 273K.

$\Delta_{s \rightarrow l} \bar{H}$ and $\Delta_{s \rightarrow l} \bar{V}$ will vary with temperature. Using the point-slope form for a straight line about the point (1 atm, 273.15K) we arrive at the equation,

$$P - P_1 = \frac{dP}{dT} (T - T_1), \quad P - 1 \text{ atm} = \frac{-1}{.00737} (T - 273.15), \quad \mathbf{P = -135.686T + 37061.5}$$

If one of the phases is an ideal gas, we can extend the *Clapeyron* equation into a more convenient although approximate form. Consider a liquid to vapor transformation, $\Delta \bar{V} = \bar{V}_{vapor} - \bar{V}_{liquid} \approx \bar{V}_{vapor}$. This approximation is based on the fact that the volume of a mole of gas is usually 1000 times larger than that of the liquid under the same conditions. Assuming an ideal behavior and 1 mole,

$$\Delta \bar{V} = \bar{V}_{vapor} - \bar{V}_{liquid} \approx \bar{V}_{vapor} = \frac{RT}{P} \quad \text{On substitution into the } \textit{Clapeyron} \text{ equation, we have}$$

$$\frac{dT}{dP} = T \frac{\Delta \bar{V}}{\Delta \bar{H}} = \frac{RT^2}{P \Delta \bar{H}}$$

$$\frac{dT}{dP} = \frac{RT^2}{P \Delta \bar{H}}$$

$$\frac{\Delta \bar{H}}{RT^2} dT = \frac{1}{P} dP$$

Now, as a final approximation, let $\Delta \bar{H}$ be considered constant as well. We integrate both sides.

$$\frac{\Delta \bar{H}}{R} \int_{T_i}^{T_f} \frac{1}{T^2} dT = \int_{P_i}^{P_f} \frac{1}{P} dP$$

$$\mathbf{-\frac{\Delta \bar{H}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right) = \ln \left(\frac{P_f}{P_i} \right)}$$

The above is the *Clausius-Clapeyron* equation

We now set out to construct a phase equilibrium diagram using the above result, along with the result of Example 6.

Example 7. How does the equilibrium vaporization temperature of pure water vary as a function of pressure?

Our reaction is: $H_2O(liq) \rightarrow H_2O(vap)$

The *Clausius-Clapeyron* equation will be used to solve this problem. First, the required data is collected.

For one mole of H_2O at 1 atm, 373K, from Table I.,

$$\Delta_{l \rightarrow v} \bar{H} = \frac{539 \text{ cal}}{\text{gram}} \frac{18 \text{ gr}}{\text{mole}} \frac{.08205 \text{ liter atm}}{1.986 \text{ cal}} = \mathbf{400.8 \text{ liter atmospheres/mole}}$$

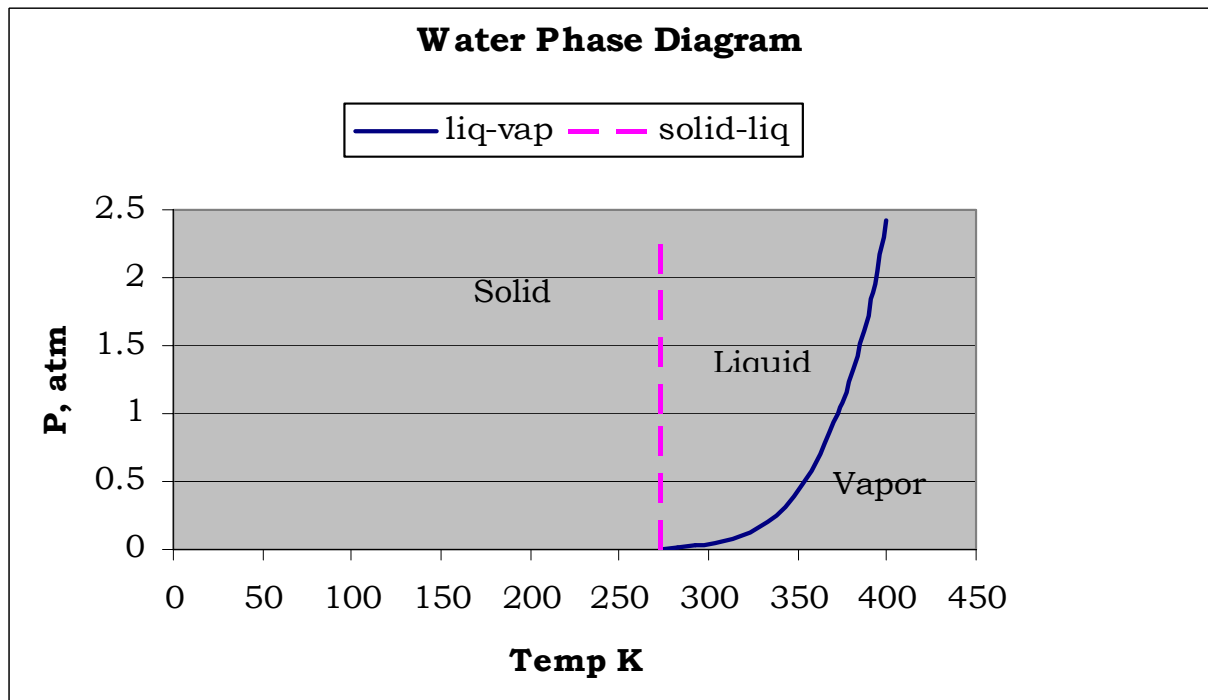
We choose the initial point at 373.15K, 1 atm. Our equation becomes,

$$-\frac{400.8 \text{ atm/mole}}{.08205 \text{ atm/moleK}} \left(\frac{1}{T_f} - \frac{1}{373.15 \text{ K}} \right) = \ln \left(\frac{P_f}{1 \text{ atm}} \right)$$

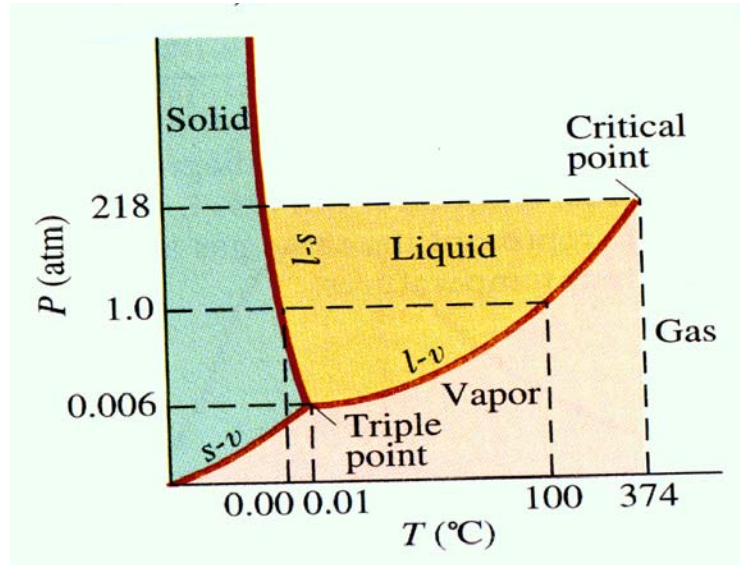
$$P_f = \exp \left(-4885 \left(\frac{1}{T_f} - \frac{1}{373.15 \text{ K}} \right) \right)$$

Above, we have an approximate relationship, in the vicinity of 373K, for the variation of boiling temperature with pressure.

Below is the equilibrium phase diagram for the H_2O system. The curves are computed from the results of Example 6 and Example 7, and are drawn to scale.



At the scale presented, it is impossible to resolve the solid-vapor line, as well as the negative slope of the solid-liquid line. Most texts on the subject present a sketch of this phase diagram using a highly distorted (artistic) scale to convey these ideas.



Above is an example of an “artistic” H₂O phase diagram. Observe that both scales are distorted. The distance from .006 to 1 atmosphere appears identical to the distance from 1 to 218 atm. Likewise, the distance from 0K (-273C) to 273K (0C) is half of the distance from 273K (0C) to 373K (100C).

Phase diagrams, in what ever form, do convey much information. Above, one can clearly see that as the pressure is increased, the liquid region is widened for H₂O; the freezing temperature decreases while the boiling temperature increases. It should be understood that the negative slope of the solid-liquid curve is highly unusual. Most materials solid-liquid curve have a positive slope. That is, most materials elevate both the freezing and boiling temperatures with increased pressure. Water is unusual in this respect.