11 Thermodynamics and Thermochemistry

Thermodynamics is the study of heat, and how heat can be interconverted into other energy forms. In thermodynamics the **system** is a specific part of the **universe** that is being studied, often the system is a chemical reaction. The **surroundings** are all parts of the universe that are not the system, typically everything outside the test tube.

- An **open** system can exchange both energy and matter with its surroundings. An active volcano is an example of an open system.

- A **closed** system can exchange energy but not matter. A sealed greenhouse is a closed system.

- An **isolated** system can exchange neither energy nor matter. A sealed thermos bottle is a isolated system.

Properties of a system which depend only on the final and initial conditions of that system are called **state functions.** State functions are independent of the path which is taken to go from an initial state to the final state. The state functions we will be working with this chapter are listed below:

P, pressure; V, volume; T, temperature; E, internal energy;

H, enthalpy; S, entropy; G, free energy.

11.1 The First Law of Thermodynamics

The first law states that energy can't be created or destroyed. In other words, when a system gains or losses energy from the surroundings, the total energy (i.e., the energy of the universe) will be constant. This is concept is expressed mathematically as:

$$\boxed{\Delta E = q + w}.$$

The E (a.k.a. U) represents the **internal energy**, this includes, but is not limited to, all kinetic and potential energy possessed by all components of a system. ΔE is the change in the internal energy of a system as the result of heat flow and work. Heat flow is indicated by q, and work done by the system is w.

The conventions that apply to the above equation are:

- q is a *positive* value if heat is *absorbed* by the system,

- q is a *negative* value if heat is lost *by* the system,

- w is a *positive* value if work is done *on* the system,

- w is a *negative* value if work is done *by* the system.

question ►

A system gains 100 calories of heat and does 75 calories of work, what is the change in the internal energy of the system?

solution:

Since heat is absorbed by the system the value for q is +100 cal. The value for w is -75 cal because the work is done by the system. Substituting into the equation gives, $\Delta E = +100 + (-75)$. $\Delta E = +25$ cal.◆

Work

We previously defined **work**, *w*, as force times displacement. Now we will look at an alternative definition. The work done by a system is equal to the negative value of the external pressure multiplied by the change in volume of the system.

$$\boxed{Work = -P\Delta V}$$

Equation 11.1

Based on Equation # we see that when a system's volume increases, it is (*by definition*) proforming negative work. (↓ Remember *by definition* means there's no reason why it couldn't have been positive—in fact a few years ago it was!)

question ►

A system expands from an initial volume of 1.0 m³ to 4.0 m³ against a pressure of 10^{-5} Pa. What is the work done by the system?

solution:

$W = -P\Delta V$, $W = -(10^{-5}$ Pa$)(4.0$ m³ $- 1.0$ m³$)$, $W = -3.0 \times 10^{-5}$ J.◆

↓ *If you check out an older text you might discover that the first law used to be defined as "$\Delta E = q - w$" and work as $+P\Delta V$. Don't Panic! The MCAT-People will use the newer definition and will not ask any questions which could be misinterperited because of this change—I hope!*

Constant Conditions

Here's a list of how the first law behaves when various conditions are held constant.

- Under conditions of constant volume $\Delta V = 0$. Since $W = P\Delta V$, $W = 0$ and $\Delta E = q$.

- When there is no heat flow heat flow, $q = 0$, and $\Delta E = -w$.

- When the temperature of a gaseous system is constant, $\Delta E = 0$ and $q = w$. Recall that the internal energy is directly proportional to its temperature.

- When the external pressure remains unchanged, q is referred to as the the change in enthalpy, *ΔH*. Under these conditions the first law may be rewritten as $\Delta E = \Delta H - P\Delta V$. In a chemical reaction in which the number of moles of gas is constant, $\Delta V = 0$, and $\Delta E = \Delta H$.

question ►

In which of the following reactions will the value for ΔE be greater than that of ΔH?

A. $CaCN_2(s) + 3 H_2O(l) \longrightarrow CaCO_3(s) + 2 NH_3(g)$

B. $3 H_2(g) + N_2(g) \longrightarrow 2 NH_3(g)$

C. $UO_2(s) + 4 HF(l) \longrightarrow UF_4(s) + 2 H_2O(l)$

D. $H_2(g) + I_2(g) \longrightarrow 2 HI(g)$
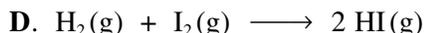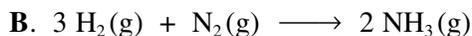
solution:

From $\Delta E = \Delta H - P\Delta V$ it is clear that if the value for work, $P\Delta V$, is negative, ΔE will be greater than ΔH. For any reaction that consumes more moles of gas than it produces the value for ΔV will be negative. Answer choice B produces 2 moles of gas while consuming four moles of gas. Its final volume is less than its initial volume. This results in a negative value for work and a value for $\Delta E > \Delta H$. So answer *B* is correct.

Answer *A* results in positive work, so $\Delta E < \Delta H$. Since there are no gases in answer *C*, w = 0 and $\Delta E = \Delta H$. Since there is no change in the number of moles of gas in answer *D* no work is done and $\Delta E = \Delta H$.◆

11.2 Enthalpy

Enthalpy, *H,* is a state function used to describe the heat changes that occur in a reaction under constant pressure. When a reaction is allowed to take place in an open container a quantity of heat proportional to the quantity of matter present, will be released or absorbed. This flow of heat is the **enthalpy change**, ΔH. The units for ΔH are kJ (or kJ/mol).

■ Reactions that release heat are termed **exothermic**, they have *negative* values of ΔH.

■ Reactions that absorb heat are termed **endohermic**, they have *positive* values of ΔH.

The endothermic reaction shown below indicates that 92.2 kJ are absorbed when 2 moles of NH_3 decompose to form 1 mole of N_2 and 3 moles of H_2.

$$2\ NH_3(g) \longrightarrow N_2(g) + 3\ H_2(g) \quad \Delta H = +92.2\ kJ.$$
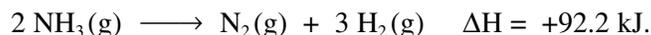
question ►

In the reaction above 100 g of NH_3 are allowed to react to produce N_2 and H_2, how many kJ of heat will be absorbed?

solution:

The reaction indicates that for every 2 moles of NH_3 consumed, 92.2 kJ will be absorbed. This information will be used in the calculation below to convert from moles of NH_3 to kJ.

$$100\ g\ NH_3\ x\ \frac{mol\ NH_3}{17\ g\ NH_3}\ x\ \frac{92.2\ kJ}{2\ mol\ NH_3}\ =\ 271\ kJ\ ◆$$

• When a reaction is reversed, the sign of ΔH is changed:

$$N_2(g) + 3H_2(g) \longrightarrow 2\ NH_3(g) \quad \Delta H = -92.2\ kJ.$$
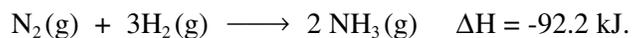
• When a reaction is multiplied through by a number, ΔH is multiplied by that same number:

$$½[N_2(g) + 3H_2(g) \longrightarrow 2\ NH_3(g) \quad \Delta H = -92.2\ kJ] =$$

$$1/2\ N_2(g) + 3/2\ H_2(g) \longrightarrow NH_3(g) \quad \Delta H = -46.1\ kJ.$$
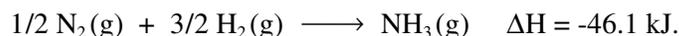
■ Good news, the above two rules work in exactly the same manner when ΔS and ΔG are involved.

Hess's Law

Hess's law states that the enthalpies of reactions may be added when these reactions are added. Substances appearing on the same side are added, while those on opposite sides are subtracted. Typically, some reactions will need to be reverse and multiplied through by a number, so that when they are combined the desired equation will result.

question ►

Find the enthalpy of the equation:

$$C_2H_2(g) + 5/2\ O_2(g) \longrightarrow 2\ CO_2(g) + H_2O(l),$$

given the following information:

(1) $2\ C_{(graphite)} + H_2(g) \longrightarrow C_2H_2(g)$ $\qquad\qquad$ $\Delta H = +226.7$ kJ

(2) $C_{(graphite)} + O_2(g) \longrightarrow CO_2(g)$ $\qquad\qquad$ $\Delta H = -393.5$ kJ

(3) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\qquad\qquad$ $\Delta H = -285.8$ kJ.

solution:

Since $C_2H_2(g)$ appears only in equation (1) it is necessary to reverse equation (1) so that the C_2H_2 appears on the left hand side to correspond to the desired equation.

Since $CO_2(g)$ appears only in equation (2), it is necessary to multiply equation (2) by two, so that two CO_2's will appear on the right hand side.

Since $H_2O(l)$ appears only in equation (3), there is no need to alter this equation since one H_2O appears on the right hand side of equation (3) and this is exactly what is required in the desired equation.

$$C_2H_2(g) \longrightarrow 2\ C_{(graphite)} + H_2(g) \qquad \Delta H = -226.7 \text{ kJ}$$

$$2\ C_{(graphite)} + 2\ O_2(g) \longrightarrow 2\ CO_2(g) \qquad \Delta H = -787.0 \text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -285.8 \text{ kJ}$$

_____

$$C_2H_2(g) + 5/2\ O_2(g) \longrightarrow 2\ CO_2(g) + H_2O(l) \qquad \Delta H = -1299.5 \text{ kJ}$$

◆
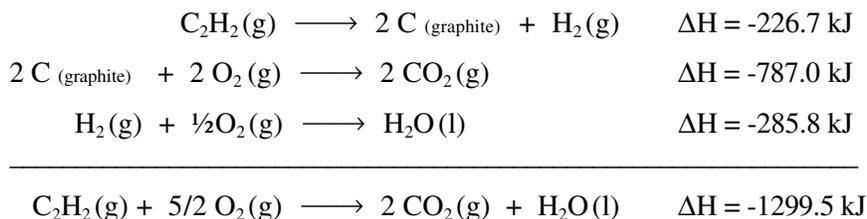
Standard Heat of Formation

A substance in its most stable form at one atmosphere is said to be in its **standard state** (the temperature need not be 25°C, but this temperature is most commonly used to tabulate data). The enthalpy change which occurs when _one mole_ of a compound is produced from its elements in their standard states is called the **standard heat of formation**, ΔH_f^o. The equation for the standard heat of formation for ammonia, NH_3, is given below:

$$1/2\ N_2(g) + 3/2\ H_2(g) \longrightarrow \underline{1}\ NH_3(g) \qquad \Delta H_f^o = -46.1 \text{ kJ}.$$
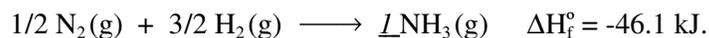
■ By definition all elements in their standard states have a ΔH_f^o equal to zero.

Standard Heat of Reaction

When all substances in a chemical reaction are in their standard states, the enthalpy change is called the standard heat of reaction, ΔH_{rxn}^o..The standard heat of reaction may be found by taking

the sum, Σ, of the standard heats of formation of the products, and subtract them from the sum of the ΔH_f°'s of the reactants. The coefficients in front of each substance must be multiplied by their respective ΔH_f°'s.

$$\Delta H^\circ_{rxn} = \left[\Sigma \Delta H_f^\circ \text{ (products)} \right] - \left[\Sigma \Delta H_f^\circ \text{ (reactants)} \right] \text{... 11.1}$$

question »

Using the above formula, find the enthalpy of the equation:

$$C_2H_2(g) + \text{5/2 } O_2(g) \longrightarrow 2\,CO_2(g) + H_2O(l),$$

given the following information:

(1) $2\,C\text{ (graphite)} + H_2(g) \longrightarrow C_2H_2(g)$ $\Delta H_f^\circ = +226.7$ kJ

(2) $C\text{ (graphite)} + O_2(g) \longrightarrow CO_2(g)$ $\Delta H_f^\circ = -393.5$ kJ

(3) $H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H_f^\circ = -285.8$ kJ
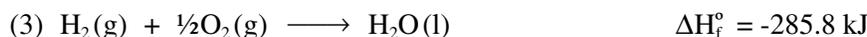
solution:

Let we let (CO_2), (H_2O), (C_2H_2), and (O_2) represent the ΔH_f° of CO_2, H_2O, C_2H_2, and O_2, respectively, we get:

$$\Delta H_{rxn}^\circ = [2(CO_2) + 1(H_2O)] - [1(C_2H_4) + \text{5/2}(O_2)]$$

$$\Delta H_{rxn}^\circ = [2(-393.5) + 1(-285.8)] - [1(+226.7) + \text{5/2}(\text{zero})] = -1299.5 \text{ kJ.}\_$$

Bond Dissociation Energy

The change in enthalpy required to break a bond is call the bond dissociation energy (or bond energy). When bonds are broken energy is absorbed. When bonds are formed energy is released. Here's the equation for the bond dissociation of hydrogen:

$$H_2(g) \longrightarrow 2\,H(g) \quad \Delta H = +435 \text{ kJ.}$$
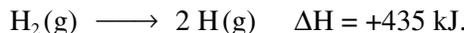
■ The larger the bond energy, the greater the bond's strength and the shorter the bond's length.

The enthalpy of a reaction may be determined by subtracting all the bond energies associated with products form those associated with the reactants:

$$\Delta H_{rxn} = \left[\Sigma \text{ Bond E. (reactants)} \right] - \left[\Sigma \text{ Bond E. (products)} \right].$$

Equation 11.2

Note that in this equation it is the bond energies of the <u>products</u> which are being subtracted. for the reactants.

question ►

Using the above formula, estimate the enthalpy of the equation:

$$C_2H_2(g) + \text{5/2 } O_2(g) \longrightarrow 2\,CO_2(g) + H_2O(l),$$

bond energies are given below in kJ/mol.

C—C	H—C	H—O	C=O	C=C	C≡C	O=O
347	414	464	803	611	837	498

solution:

> First we need to work out the structural formulas to clearly identify the number and types of bonds:
>
> $H-C\equiv C-H + 5/2\ O=O \longrightarrow 2\ O=C=O + H-O-H.$
>
> Let's, list the bonds with bond energies indicated within parenthesis, and coefficents indicating the number of bonbs of each type:
>
> $\Delta H = [2(H-C) + 1(C\equiv C)\ 5/2(O=O)] - [4(O=C) + 2(H-O)]$
>
> Finally let's put the numerical values in, then crunch the numbers:
>
> $\Delta H = [2(414) + 1(837)\ 5/2(498)] - [4(803) + 2(464)] = -1230\ kJ.$◆
>
> ►Note that *two* moles of CO_2, contain *four* moles of C=O bonds.
>
> ►Note that the bond energy of three C−C bonds does *not* equal the bond energy of one C≡C.
>
> ►Since bond energies are generally averages taken from many molecules, the result obtained for the above question is less accurate then in the two previous methods we used to determine the ΔH.

11.3 Entropy

Entropy, *S*, is a quantitative measure of the disorder or randomness of a system. The greater the number of ways that matter can be arranged, the greater entropy. Listed below are some criteria for predicting changes in entropy.

- Entropy increases with temperature.

- Solids have the lowest entropy, while gases have the most. Liquids and aqueous solutions have intermediate values.

- In any reaction where the number of moles gas increases the entropy will increase.

- When pure substances form mixtures entropy will increase.

- Reactions like, $2HI(g) \longrightarrow H_2(g) + I_2(g)$, where the number of moles of gas are constant, but the number of different types of gas increases, proceed with an increase in entropy.

The **standard absolute entropy**, S°, of a substance is the entropy of that substance in its standard state. Unlike standard enthalpies, all standard entropies are nonzero values. The equation below allows the calculation of the change in entropy for a reaction.

$$\boxed{\Delta S^\circ_{rxn} = \left[\Sigma S^\circ_{(products)}\right] - \left[\Sigma S^\circ_{(reactants)}\right]}$$

The SI units for entropy are J/K (or J/K·mol).

The Second Law

Any reaction that tends to proceed forward to form products is said to be **spontaneous**. The second law states that for any spontaneous change the total change in entropy will be positive,

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0.$$

All isolated systems spontaneously tend toward equilibrium. Once a system reaches equilibrium it achieves a maximum state of entropy.

11.4 Gibbs Free Energy

The Gibbs free energy, *G*, is a measure of the energy available to the system to do useful work. The difference in free energy between the products and the reactants is called the **free energy change**, *ΔG*. ΔG is expressed in kJ (or kJ/mol). When the free energy of the reactants is greater than that of the products a reaction will be spontaneous. It is the sign of ΔG which may be used to determine the spontaneity of a reaction.

- If ΔG is negative, the reaction is spontaneous.

- If ΔG is positive, the reaction is nonspontaneous.

- If ΔG is zero, the reaction is at equilibrium.

■ Although it is the **change in free energy**, *ΔG*, which determines the direction of a reaction, it is the activation energy which determines its rate.

The value of ΔG may be obtained by the formula below if ΔH, T, and ΔS is known:

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

When using this formula the temperature must be in Kelvin, and the units of energy for ΔH and ΔS must be the same.

The relationship between ΔH, T, and ΔS as they relates to spontaneity is shown in the adjacent table. Although the values of ΔH and ΔS tend to remain constant at different temperatures, the value for ΔG is highly temperature dependent. Reactions having values of ΔH and ΔS which bear the same sign, reach equilibrium when ΔH = TΔS. At this temperature ΔG = 0

	ΔH	
	(+)	**(-)**
(+)	spontaneous at high temperatures	spontaneous
ΔS		
(-)	nonspontaneous	spontaneous at low temperatures

Since boiling and freezing are equilibrium processes ΔG = 0. Setting ΔG equal to zero and solving for temperature in ΔG° = ΔH° - TΔS° gives:

$$\text{normal BP} = \frac{\Delta H^{\circ}_{vap}}{\Delta S^{\circ}_{vap}}$$

$$\text{normal FP} = \frac{\Delta H^{\circ}_{fus}}{\Delta S^{\circ}_{fus}}$$

where is ΔH°_{vap} is the change in the enthalpy of vaporization, and ΔH°_{fus} the change in enthalpy of fusion.

Standard Free Energy of Formation

The change in free energy when one mole of a compound is made from its elements in their standard states is called the **standard free energy of formation**, ΔG_f^o. All elements in their standard states have values of ΔG_f^o equal to zero.

Standard Free Energy Change

The **standard free energy change, $\Delta G°$**, is defined as the change in free energy which results when all reactants and products are in their standard states and all solutions are at 1 M concentration. The expression below may be used to solve for $\Delta G°$ when the ΔG_f^o's for a reaction are known:

$$\Delta G_{rxn}^o = [\Sigma \Delta G_{f\,(products)}^o] - [\Sigma \Delta G_{f(reactants)}^o]$$.

Another method for obtaining $\Delta G°$ is from the equilibrium constant, K,. In the equation below, R is the gas constant and T is the temperature in K.

$$\Delta G° = -2.3RT \log K$$

$\Delta G°$ is measured under standard conditions where all gases are at 1 atm and all solutions at 1M. Under these conditions, the reaction quotient, Q, will be equal to one. It followings, therefore, that all reactions with values of K larger than one will be spontaneous under standard conditions.

*   If $K < 1$, $\Delta G° > 0$,
    the reaction will proceed toward the reactants and is nonspontaneous.

*   If $K = 1$, $\Delta G° = 0$,
    the reaction is already at equilibrium.

*   If $K > 1$, $\Delta G° < 1$,
    the reaction will proceed toward the products, and is spontaneous.

To solve for the free energy change under nonstandard conditions, you may use the equation below:

$$\Delta G = \Delta G° + 2.3RT \log Q$$.

Recall that for the reaction, $a\,A + b\,B \rightleftharpoons c\,C + d\,D$,

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}.$$

The units of concentration for gases should be in *atm* and aqueous solutions are in *M*. Pure solids and liquids do not appear in either Q or K.