Chapter 2

Thermodynamics and Kinetics Review

This chapter will refresh your memory for concepts taught in physical chemistry and general chemistry courses. You will require these ideas throughout this text.

2.1. Thermochemistry Review

Before we can discuss any relevant reactions, we must equip ourselves with the proper tools to fully understand them. Shown below are the arrows commonly used in organic chemistry schemes. We will be adhering strictly to these conventions. Please note the difference between the double-sided and one-sided arrows for pushing pairs of electrons and single electrons, respectively.

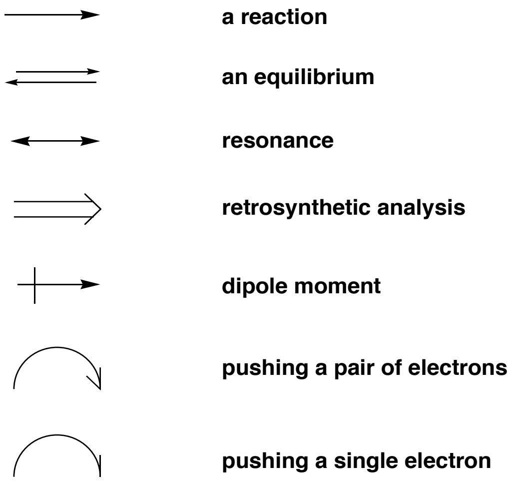


Figure 2.1. Arrows in organic chemistry.

In this text, we will assume that you are familiar with basic concepts from general chemistry. This includes enthalpy and free energy, standard molar enthalpies of formation (otherwise known as “Heats of Formation”), Le Chatelier’s Principle, application of Hess’s law and the significance of standard state.

2.1.1. UNITS

Throughout this text you will find that we frequently mix or alternate between kcal/mol and kJ/mol. The "SI" (Standard International) unit for energy is the *Joule* (abbreviated "J") and energy changes associated with reactions should then be expressed in kJ/mol. However, the reality is that in your professional careers you will find that non-SI units are frequently employed. Getting used to working with many units is an important aspect of your education. Therefore, it is important to know the following relationship between calories and joules:

$$1 \text{ cal} = 4.184 \text{ J}$$

Equation 2.1

2.1.2. HEATS OF FORMATION

If you understand the basic concepts of thermochemistry mentioned previously, then solving the following problem should be straightforward:

> Knowing the heat of formation of gaseous ethane (+52.3 kJ/mol) and carbon dioxide (gas, -110.5 kJ/mol) and water (liquid, -285.8 kJ/mol), calculate the heat of combustion of ethane in kcal/mol.
>
> *Answer: -270.5kcal/mol (- 1130.7 kJ/mol)*

In fact, heats of formation are frequently derived from combustion studies, as in the following example for methane.

$$CH_4(g) + 2\ O_2(g) \longrightarrow CO_2(g) + 2\ H_2O(l) \qquad \Delta H_R = -890.0 \text{ kJ/mol}$$

Scheme 2.1. The combustion of methane.

A few things should be noticed; first, the value of ΔH_R is negative, meaning the reaction is exothermic, as combustions are expected to be; second, each compound is labelled with (g) or (l) indicating they are gases or liquids, respectively. The value of ΔH_R for a given reaction changes if the reagents or products are in a different state of matter, for example, if water in the example of Scheme 2.1 was included as a gas. The participants in our example have all been included in their standard state, i.e. in their normal form at 25ºC and 1 bar pressure. Now we express the value in terms of the enthalpies of formation of the reaction participants:

$$\Delta H_R = +\underset{\textbf{products}}{(\Delta H_f\,(CO_2) + 2\ \Delta H_f\,(H_2O))} - \underset{\textbf{reactants}}{(\Delta H_f\,(CH_4) + 2\ \Delta H_f\,(O_2))}$$

Equation 2.2

For the purposes of our example we will assume that the value of ΔH_f (CH_4) is unknown, while all the others are available in the literature. Note also that the stoichiometric factors (the '2' for water and oxygen) also appear in the equation. We now enter the known information:

$$-\ 890.0 \text{ kJ/mol} = +\ (-393.5 \text{ kJ/mol} + 2 \times (-285.8 \text{ kJ/mol})) - (\Delta H_f\,(CH_4) + 2 \times 0)$$

Equation 2. 3

From this expression, we obtain $\Delta H_f(CH_4)$ = +75.1 kJ/mol = +18.0 kcal/mol.

Note that 75.1 kJ/mol actually converts to 17.9665 kcal/mol, which we round up to 18.0 kcal/mol. Use of a meaningful number of significant figures is important. In this case there is no reason to use more than the one decimal figure (given the precision of the starting value).

Also note that the enthalpies of formation for water and carbon dioxide are both negative, as they should be, since they correspond to the enthalpies of combustion for hydrogen and carbon, respectively. Note also that the value for oxygen is zero. The enthalpies of formation for all the elements in the standard state are zero for the most stable allotrope (in this case for oxygen, but not for ozone).

For the reaction written as:

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$$

The value of ΔH_R is –802.4 kJ/mol. Can you explain quantitatively the origin of the difference between this value and -890.0 kJ/mol given above?

2.1.3. THE VAN'T HOFF EQUATION

In addition to Hess's Law and heats of formation, you should be familiar with the following expression relating the Gibbs' free energy change of a reaction to the enthalpy and entropy changes in the standard state:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad \text{Equation 2.4}$$

However, the Gibbs' free energy can also be expressed as a function of the equilibrium constant, K_{eq}:

$$\Delta G^o = -RT\ln K_{eq} \qquad \text{Equation 2.5}$$

From these two equations, we obtain the following expression for the equilibrium constant:

$$\ln K_{eq} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad \text{Equation 2.6}$$

Thus, a plot of $\ln K_{eq}$ against $1/T$ will yield a straight line with a slope of $-\Delta H^o/R$ and a y-axis intercept of $\Delta S^o/R$.

Over moderate ranges of temperature, it is possible to neglect any temperature dependence in ΔH^o and $-\Delta S^o$ (*i.e.* we may assume that these values are constant). Thus, given an equilibrium constant at a specific temperature (K_1 at T_1), we are able to determine the equilibrium constant at another temperature (K_2 at T_2):

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^o}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \text{Equation 2.7}$$

This expression is known as the van't Hoff equation.

For the hypothetical equilibrium $A \leftrightarrows B$, you obtain the following data.

T (K)	K_{eq}
260	6.2×10^{-2}
280	1.6×10^{-2}
300	5.2×10^{-3}
320	1.9×10^{-3}

Determine the values of ΔG°, ΔH°, and ΔS°. What would be the equilibrium constant at T = 325 K?

Answer: 13 kJ/mol, -40 kJ/mol, -177 J/mol, 1.5×10^{-3}.

2.1.4. BOND DISSOCIATION ENERGIES (BDE)

Bond dissociation energies (also referred to as "bond strengths" or "bond energies", and abbreviated BDE) refer to the enthalpy change associated to the homolytic cleavage of one bond in a molecule. They are normally expressed for the gas phase reaction under standard conditions (25°C, 1 bar). Scheme 2.2 gives two examples; first, the case of hydrogen and, second, the case of a slightly more complex molecule, ethane.

$$H_2(g) \longrightarrow 2\,H\bullet\,(g) \qquad \Delta H = +\,104.2\ \text{kcal/mol} \quad +\,435.6\ \text{kJ/mol}$$

$$C_2H_6\,(g) \longrightarrow 2\,CH_3\bullet\,(g) \qquad \Delta H = +\,(88 \pm 1)\ \text{kcal/mol} \quad +\,368\ \text{kJ/mol}$$

Scheme 2.2. Bond dissociation energies for hydrogen and ethane.

The enthalpy of formation of the hydrogen atom is +52.1 kcal/mol, or exactly one half of the bond dissociation energy for the hydrogen molecule. However, the enthalpy of formation for the methyl radical ($CH_3\bullet$) is +34.3 kcal/mol, which does <u>not</u> correspond to one half of the BDE for ethane. Explain.

Note the positive sign (+) in front of the enthalpies given above. This indicates that the process is endothermic, *i.e.* it requires energy input to occur. In general, we will not place the + sign as above; we will assume the values are positive unless indicated otherwise.

The following table provides some useful representative values for bond dissociation energies. Note that these are typical values, but do not apply exactly to every molecule. For example the value for C–H is given as 413 kJ/mol; this value happens to be approximately that corresponding to the C–H bond in ethane. However, we expect the C–H bond in methane to be stronger, while a tertiary C–H bond will be weaker.

Table 2.1. Representative values for bond dissociation energies (values given in kJ/mol).

Single bonds

Bond	BDE	Bond	BDE	Bond	BDE	Bond	BDE
C-H	413	N-H	391	O-H	463	F-F	155
C-C	348	N-N	163	O-O	146		
C-N	293	N-O	201	O-F	190	Cl-F	253
C-O	358	N-F	272	O-Cl	203	Cl-Cl	242
C-F	485	N-Cl	200	O-I	234		
C-Cl	328	N-Br	243			Br-F	237
C-Br	276			S-H	339	Br-Cl	218
C-I	240	H-H	436	S-F	327	Br-Br	193
C-S	259	H-F	567	S-Cl	253		
		H-Cl	431	S-Br	218	I-Cl	208
Si-H	323	H-Br	366	S-S	266	I-Br	175
Si-Si	226	H-I	299			I-I	151
Si-C	318						
Si-O	368						

Multiple bonds

Bond	BDE	Bond	BDE	Bond	BDE
C=C	614	N=N	418	O=O	495
C≡C	839	N≡N	941		
C=N	615			S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

2.1.5. GROUP CONTRIBUTIONS

The heats of formation of organic molecules vary systematically with their molecular structure. This is nicely illustrated in the following figure for hydrocarbons, primary alcohols and other molecules (many other types of molecules also yield similar correlations).

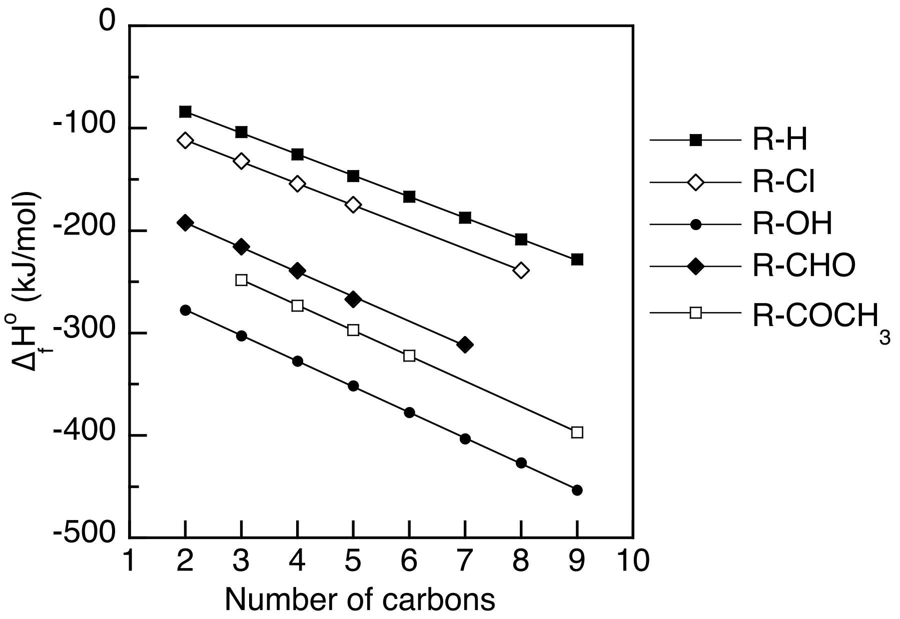
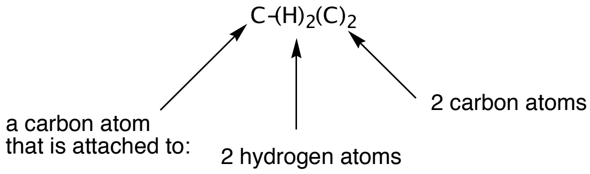


Figure 2.2. Enthalpies of formation for simple organic molecules: alkanes, chloroalkanes, primary alcohols, aldehydes, and methyl ketones.

Note that all plots yield an excellent straight line; further, the lines are essentially parallel, indicating that each CH_2 group makes the same contribution to Δ**H°** (-20.7 kJ/mol, or -4.93 kcal/mol) regardless of the terminal functional group. Benson has developed this simple concept and estimated "group contributions" for a large number of moieties.

Thus the *group contribution* for CH_2 is –4.93 kcal/mol. However, if you look closely at the plot above, you will notice that the CH_2 groups added have something in common, they are all between two carbon atoms. We need to be able to 'label' the group, so that in using it later we will know if the values were derived for groups in the same molecular environment. For the above example the label would be the one presented in Scheme 2.3.



Scheme 2.3. Labelling a CH_2 according group additivity rules.

There are some cases where other conditions come into play. For example, both cyclopropane and cyclohexane contain exclusively CH_2 groups. Simple addition of CH_2 contributions works well for cyclohexane, but not for cyclopropane. To illustrate this discrepancy, perform the following calculation:

The experimental heats of formation for cyclopropane and cyclohexane are +53.3 and -123.1 kJ/mol, respectively. Estimate the heats of formation based on the additivity of CH_2 properties and discuss the difference.

What we have just discovered (see box above) is called *ring strain*, a factor which must be considered in many reactions of cycloalkanes.

A particularly important reaction mentioned throughout this text is combustion. Here, ring strain is reflected in the fact that combustion of two moles of cyclopropane releases more energy than combustion of one mol of cyclohexane. Table 2.2 gives combustion data for a series of cycloalkanes.

Table 2.2. Combustion data for cycloalkanes

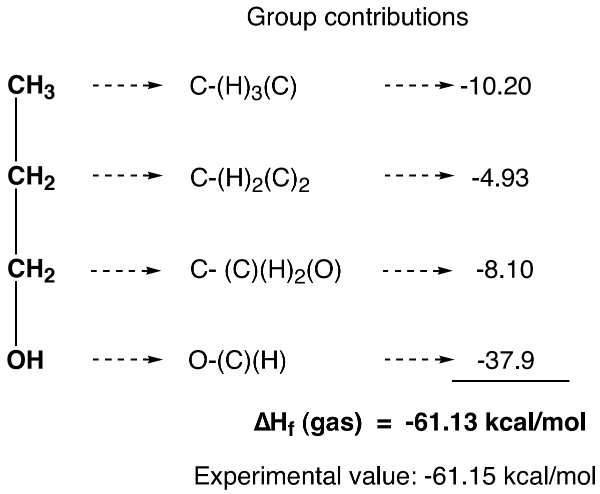
Cycloalkane	CH_2 units	ΔH_{comb} 25ºC	ΔH_{comb} 25ºC per CH_2 unit	Ring Strain
$(CH_2)_n$	n	kcal/mole	kcal/mole	kcal/mole
Cyclopropane	n = 3	468.7	156.2	27.6
Cyclobutane	n = 4	614.3	153.6	26.4
Cyclopentane	n = 5	741.5	148.3	6.5
Cyclohexane	n = 6	882.1	147.0	0.0
Cycloheptane	n = 7	1035.4	147.9	6.3
Cyclooctane	n = 8	1186.0	148.2	9.6
Cyclononane	n = 9	1335.0	148.3	11.7
Cyclodecane	n = 10	1481	148.1	11.0

Notice that the values for ΔH_{comb} 25^{o}C per CH_2 unit are directly proportional with the ring strain of the corresponding molecules.

Below are two examples of the labelling found in Table 2.3 and how to interpret them:

- $C\text{-}(C_d)(C)(H)_2$ means that a carbon atom has 4 substituents; one is a carbon that is part of a double bond, another is an sp^3 carbon, and two are hydrogen atoms.
- $C\text{-}(H)_3(O)$ represents a carbon atom connected to an oxygen (with a single bond) and to three hydrogens, *e.g*. as in methanol.

Scheme 2.4 shows an example of the calculation of the heat of formation for 1-propanol; all values were obtained from Table 2.3.



Scheme 2.4. Calculating ΔH_f for 1-propanol using group additivity rules.

Group contributions are available not just for enthalpy, but also for entropy and specific heat capacity. We will only be concerned with the use of enthalpies to calculate heats of formation of interesting molecules. Table 2.3 gives a selection of values for molecules containing C, H and O. Note the special designations for sp^2 hybridized carbons (C_d) and sp hybridized carbons (C_t); as well, in your calculations, note that the carbonyl group (CO) is treated as a single group.

Table 2.3. Selected Enthalpic Contributions-kcal/mol for Different Groups (from: Benson, S. W. *Thermochemical Kinetics*; 2nd Ed. ed.; Wiley: New York, 1976.)

Group	Value (kcal/mol)	Group	Value (kcal/mol)	Group	Value (kcal/mol)
C-$(H)_3$ (C)	-10.20	C-(C_d)(C)$(H)_2$	-4.76	O-(C)(H)	-37.9
C-$(H)_2$$(C)_2$	-4.93	C-(C_t)(C)$(H)_2$	-4.73	O-(C_d)(H)	-37.9
C-(H)$(C)_3$	-1.90	C-(C_d) $(C)_2$ (H)	-1.48	O-(C_t)(H)	-37.9
		C-(C_t)(H)$(C)_2$	-1.72		
C- $(C)_4$	0.50	C-$(H)_3$(O)	-10.1	O-(O)(H)	-16.3
		C-$(H)_2$(C)(O)	-8.1	O-(CO)(H)	-58.1
C_d-(H_2)	6.26	C-$(H)_2$$(O)_2$	-16.1	O-$(C)_2$	-23.2
C_d-(H)(C)	8.59	C-(O)(H)$(C)_2$	-7.2	O-(C_d)(C)	-30.5
C_d-$(C)_2$	10.34	C-$(C)_3$(O)	-6.6	O-(C)(O)	-4.5
C_t-(H)	26.93	C-(H)(C)$(O)_2$	-16.3	O-(CO)(C)	-43.1
C_t-(C)	27.55	C-$(C)_2$$(O)_2$	-18.6	O-$(CO)_2$	-46.5
		C-$(C_d)$$(H)_3$	-10.0		
Ring Corrections		C-$(H)_3$(CO)	-10.1	CO-$(H)_2$	-26.0
cyclopropane	27.6	C-$(H)_2$(C)(CO)	-5.2	CO-(H)(C)	-29.1
cyclobutane	26.2	C-(H)$(C)_2$(CO)	-1.7	CO-$(C)_2$	-31.4
cyclopentane	6.3	C-$(C)_3$(CO)	1.4	CO-$(O)_2$	-29.9
cyclohexane	0	C-$(H)_2$$(CO)_2$	-7.6	CO-(C)(O)	-35.1
cycloheptane	6.4	C-(H)(C)$(CO)_2$	-5.4	CO-(H)(O)	-32.1

Abbreviations: C_d = sp^2 carbon centre; C_t = sp carbon centre; CO = carbonyl group

2.2 Kinetics Review

Many aspects of applied chemistry, and in particular polymer chemistry, rely heavily on our understanding of chemical kinetics. Although basic knowledge of concepts will be assumed, this section will serve as a *brief* reminder of topics covered in physical chemistry texts. Specific aspects regarding free radical chain reactions are discussed in subsequent chapters.

2.2.1. REACTION COORDINATE DIAGRAMS

You should be familiar with reaction coordinate diagrams displaying activation energies and transition states. Figure 2.3 illustrates a generic energy profile for a hypothetical exothermic reaction. Two activation energies are shown in Figure 2.3: $E_{a\,(fwd)}$ is the activation energy for the forward reaction ($A+B \rightarrow C+D$), and $E_{a\,(rev)}$ is that for the reverse reaction ($C+D \rightarrow A+B$).

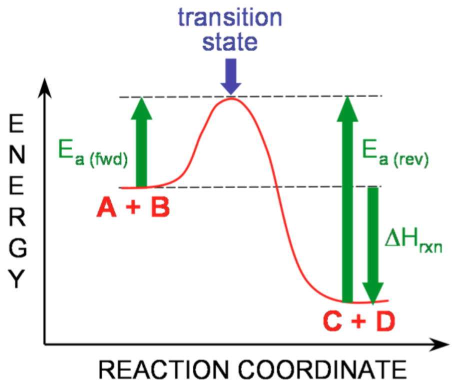


Figure 2.3. Simplified reaction profile for an exothermic reaction.

From this profile, a simple relationship between the enthalpy of the reaction (ΔH_{rxn}) and the activation energies can be derived:

$$\Delta H_{rxn} = E_{a\,(fwd)} - E_{a\,(rev)} \qquad \text{Equation 2. 8}$$

In the case of Figure 2.3, the value of ΔH_{rxn} obtained from this expression would be *negative*, reflecting the fact that this is an exothermic reaction, where heat is released to the surroundings.

Redraw Figure 3 for an endothermic reaction, showing ΔH_{rxn}, $E_{a\,(fwd)}$, and $E_{a\,(rev)}$.

Reaction profiles are affected by the presence of catalysts. By definition, a catalyst is a substance that accelerates the rate of a reaction without itself being consumed. Catalysts increase the rate by providing an alternate pathway for the reaction to follow – sometimes, simply by providing a surface upon which reactant molecules can come together to react. The result is a lowering in the position of the transition state barrier in the reaction profile and a corresponding decrease in the size of the activation energy.

Note, however, that catalysts do *not* alter the relative thermodynamic positioning of the reactants or products; catalysts therefore have no effect on the overall thermodynamics of a system. Because of this fact, catalysts cannot change the equilibrium point of a reaction, they can only get the reaction to reach the equilibrium point *faster*. We shall see several examples of catalytic cycles throughout this text.

2.2.2. THE ARRHENIUS EQUATION

The effect of temperature and activation energy on a rate constant is expressed by the Arrhenius equation,

$$k = A \times e^{-\frac{E_a}{RT}} \qquad \text{Equation 2.9}$$

where R is the gas constant (8.3145 J mol^{-1} K^{-1}) and A is known as the pre-exponential factor. The pre-exponential factor has the same units as k: s^{-1} for first order reactions and $\text{M}^{-1}\text{s}^{-1}$ for second-order reactions. Values for A are typically large and reflect entropic factors.

The Arrhenius equation follows the experimental observations of increasing rate with increasing temperature and/or decreasing activation energy. This expression can be used to determine activation energies by measuring the rate constant of a reaction at different temperatures. By taking the natural logarithms of both sides of the equation, we obtain

$$\ln k = \ln A - \frac{E_a}{RT} \qquad \text{Equation 2.10}$$

Thus, if the Arrhenius law applies, a plot of ln k versus $1/T$ will yield a straight line, with a y-axis intercept equal to ln A and a slope equal to $-E_a/R$. Much like ΔH° and ΔS° in the van't Hoff equation, we can assume the value of E_a to be temperature independent over small temperature ranges, and thus given a rate constant at a specific temperature (k_1 at T_1), we are able to determine the rate constant at another temperature (k_2 at T_2):

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \text{Equation 2.11}$$

Interestingly, the Arrhenius equation has applications beyond elementary chemical reactions. For example, it has been shown that the rate of cricket chirps, firefly flashes, and many other biological processes follow this behaviour.

2.2.3. RATE EXPRESSIONS

The rate constants 'k' used in the expressions above are derived from experimental rate data on either product formation or reagent consumption. This section deals with the relationships from which 'k' values can be derived.

The rate of a chemical reaction is defined as the change in concentration of a reactant or product in a given unit of time. For example, for the following reaction (where a, b and c and stoichiometric coefficients):

$$\text{aA} + \text{bB} \rightarrow \text{cC} \qquad \text{Equation 2.12}$$

we can write the rate of the reaction as

$$Rate = -\frac{1}{a} \times \frac{d[A]}{dt} = -\frac{1}{b} \times \frac{d[B]}{dt} = +\frac{1}{c} \times \frac{d[C]}{dt} \qquad \text{Equation 2.13}$$

The negative sign reflects the *depletion* of starting materials A and B whereas the positive sign indicates the *accumulation* of product C.

The equation above relates the changes of concentration with time for the reagents and products. The *rate expression* gives us the form for that dependence, *e.g.,* for the reaction above, we may see an expression such as:

$$Rate = k[A]^a[B]^b \qquad \text{Equation 2. 14}$$

where k is the *rate constant* for the reaction and the exponents 'a' and 'b' coincide with the stoichiometric factors if the reaction corresponds to an elementary reaction step (see below). These numbers are known as the *order of reaction* with respect to a reactant; sometimes referred to as the *partial order*. For example, a is the order of reaction with respect to reagent A. These orders are determined experimentally and may not always be whole numbers. The sum of all partial orders ($a + b + ...$) is known as the *overall order* and is usually denoted with the symbol n.

In complex reactions (*e.g.* free radical reactions) the relationship between the orders of reaction and the stoichiometric factors follows a complex dependence. We will learn more about some of these in Chapter 3.

2.2.4. MOLECULARITY AND ORDER

In the section above, we examined an 'elementary' reaction and defined the order of reaction. However, in this text, we will be introducing more complex reactions, which are composites of many individual reaction steps. Therefore, it is necessary to be able distinguish between the *order* and the *molecularity* of a reaction.

Suppose you are presented with an equation describing the overall stoichiometry for a chemical reaction, such as

$$\mathrm{A + B \rightarrow C} \qquad \text{Equation 2.15}$$

However, this seemingly simple overall reaction may not, in fact, represent the actual mechanism by which the transformation takes place. For instance, the overall reaction could occur by the following two-step mechanism:

$$\mathrm{A \rightarrow I} \qquad \text{Equation 2.16}$$

$$\mathrm{I + B \rightarrow C}$$

where I is an intermediate species. When an overall reaction is broken down into individual steps, these steps are known as *elementary reactions* – they cannot be sub-divided or derivatized any further.

Once a reaction has been identified as an elementary reaction, then one may comment on its *molecularity*: that is, how many molecules enter the reaction step. In the mechanism described in Equation 2.16, the first step would then be a *unimolecular reaction*, whereas the second step is a *bimolecular reaction.*

It is critical that you understand the difference between molecularity and order: the order of a reaction is an experimentally observed value representing an overall reaction, whereas the molecularity of a reaction reflects the number of molecules participating in a given reaction mechanism step.

However, knowing the molecularity of an elementary step does allow us to comment on the order of that step. In general, if an elementary step is unimolecular, than the reaction is first-order with respect to the reactant. In our mechanism described above (Equation 2.16), the first step is then a first-order reaction, and we can write the rate expression as

$$Rate = -\frac{d[A]}{dt} = k[A] \qquad \text{Equation 2.17}$$

Similarly, for bimolecular elementary steps we can write second-order rate expressions. Following our example above, we obtain:

$$Rate = -\frac{d[I]}{dt} = -\frac{d[B]}{dt} = k[I][B] \qquad \text{Equation 2.18}$$

Notice that molecularity and order is a ‘one-way street’: we can say that a unimolecular reaction will be first-order, but we cannot say that an overall reaction observed to be first-order will be unimolecular.

2.2.5. KINETIC EQUATIONS

We will not repeat here the derivations of kinetic expressions already well described in general and physical chemistry textbooks. Instead, Table 2.4 provides a review of the equations and concepts that will be needed.

Table 2.4. Basic Kinetic Concepts

	1^{st} Order	**2^{nd} Order**
Rate Law	= k[A]	= k[A][B] or $k[A]^2$
Half-life	$t_{1/2} = \frac{\ln 2}{k} = \frac{0.69}{k}$	$t_{1/2} = \frac{1}{kc}$
Lifetime	$\tau = 1/k$	Not used
Units of k	Time^{-1}	$\text{Conc}^{-1}\text{Time}^{-1}$
Common units for k	s^{-1}	$M^{-1}s^{-1}$
Integration	$\frac{dc}{c} = -k\ dt$	$\frac{dc}{c^2} = -k\ dt$
Dependence of conc with time	$\ln\left(\frac{c}{c_0}\right) = -kt$	$\frac{1}{c} - \frac{1}{c_0} = kt$
Plot to get k	ln c vs. time	1/c vs. time
Variation of half-life with decreasing concentration	Invariant, no change in τ or $t_{1/2}$ with time	Life gets longer as concentration decreases

Note that the "lifetime", or τ relates to the time required for the reactant concentration to decrease by "1/e" (where e = 2.718…), and corresponds to 36.8% of the initial reagent remaining. The concept is not utilized in the case of higher order reactions (such as second order). For a first order reaction the "lifetime" is independent of the initial reagent concentration …. *but this is only for a first order reaction!*

2.3 For Further Reading

K. J. Laidler and J. H. Meiser. Physical chemistry. Boston : Houghton Mifflin, 1999.

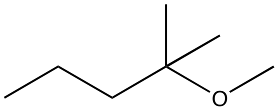
P. Atkins and J. DePaula. Physical chemistry. New York : W.H. Freeman, 2002.

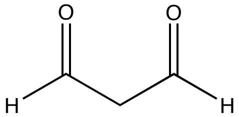
Benson, S. W. Thermochemical Kinetics 2nd Ed. New York: Wiley, 1976.

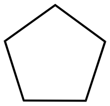
2.4 Study Questions

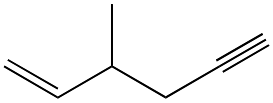
1) The standard heat of formation of solid potassium chlorate is -835 kJ. Write the chemical equation for the reaction to which this value applies.

2) Using Table 1, calculate the group additivities for the following compounds:









Answers: -80.36, -65.8, -18.35, +52.92 kcal/mol

3) For a hypothetical reaction A + B → C + D, the activation energy is 32 kJ/mol. For the reverse reaction, the activation energy is 58 kJ/mol. Is the reaction exothermic or endothermic?

4) Using a table of free energies of formation (found in any general chemistry text) decide if the combustion of liquid benzene would be thermodynamically favourable. Is this a *spontaneous* process? Why or why not?

5) A first order reaction is 40% complete in 1 hour. What is the value of the rate constant? In how long will the reaction be 80% complete?

Answers: $1.42\times10^{-4}s^{-1}$*, 189 min*

6) Calculate the activation energy for the reaction:

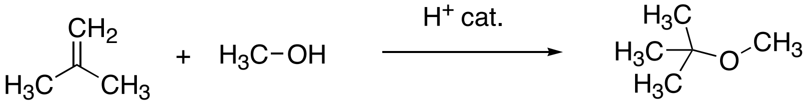
$$N_2O_5(g) \rightarrow 2\ NO_2(g) + 1/2\ O_2(g)$$

where k at 25°C is $3.46 \times 10^{-5}\ s^{-1}$, and k at 55 °C is $1.5 \times 10^{-3}\ s^{-1}$.

Answer: 100 kJ/mol

7) For a given reaction, the plot of lnK versus 1/T yields a slope of - 13.9 and a y-intercept of 2.6×10^{6}. Knowing this information, determine the relative signs (+ or –) of each of the following values, if possible: ΔH^o, ΔS^o, ΔG^o, E_a, A.

8) Using group additivity values, estimate the ΔH^o of the following reaction.



9) If you plot the inverse of concentration (1/c) as a function of time for a given chemical reaction and obtain a straight line, what is the overall order of the reaction?

10) Write a rate expression for the following elementary step: $A + B \rightarrow 2\ C$