Fundamentals of Theoretical Organic Chemistry

Lecture 1

1 Introduction

Most of the organic compounds have a structurally well defined carbon skeleton, frequently denoted by R (the first letter of the word: Radical) and carry a single functional group (G)

$$R - G$$

1.1.1—1. eq.

Simple examples of these molecular structures are:

$$R - Cl \quad \text{An organic halide}$$

1.1.1—2. eq.

$$R - OH \quad \text{An organic alcohol}$$

1.1.1—3. eq.

The purpose of classical organic chemistry is to study the structure of organic molecules and the reaction which interconverts one organic structure to another. These interconversions or chemical reactions need some reagents which may be inorganic or organic:

$$\text{Structure}_1 \xrightarrow{\text{Reagent}} \text{Structure}_2$$

1.1.1—4. eq.

$$R - G_1 \xrightarrow{\text{Reagent}} R - G_2$$

1.1.1—5. eq.

$$R - Cl \xrightarrow{OH^-} R - OH + Cl^-$$

1.1.1—6. eq.

When we are dealing with the structure of organic molecules we are concerned with the architecture of the molecule and the architecture is three dimensional. The 3D-structural chemistry is frequently referred to as stereochemistry.

Molecular structure is very important not only because it is pre-requisite knowledge for organic synthesis but also because it predetermines the physical property, chemical reactivity and biological activity of the organic molecule in question. In other words the architecture or the structure of the molecules is an independent variable, while

Physical properties

1.1.1—7. eq.

Chemical reactivities

1.1.1—8. eq.

Biological activities

1.1.1—9. eq.

are dependent variables. Consequently, we can specify symbolically such functional dependence:

Property=f(structure)

1.1.1—10. eq.

Reactivity=F(structure)

1.1.1—11. eq.

Activity=f(structure)

1.1.1—12. eq.

Yet, we are not sure, at this time, of the explicit functional dependence. Thus, we may only guess on the basis of accumulated experience what molecular structure will give us a bright red color, what structural feature of a plastic may enhance chemical or biodegradability and what drug candidate could perhaps have the desired pharmacological effect. In other words, at this point in history, we are not in the position to do precise molecular engineering, i.e. to design a molecular structure that delivers the desired physical, chemical and biological characteristics. One may anticipate, at this time, that a great deal of advancement along this line will occur in the 21st century.

1.1 Experimental Background

1.1.1 Stable structures and Transition States

The term stable structure refers to the structure of a molecule with the lowest (minimum) internal energy (E) over a range of geometrical distortions, which the molecule can have.

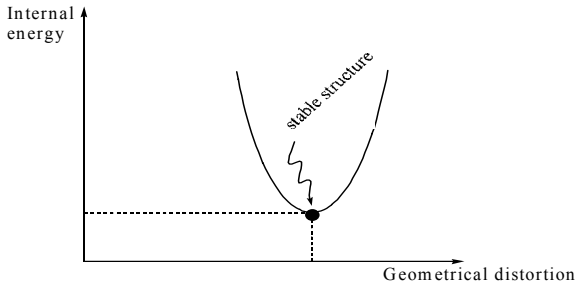


Figure. 1.1.1—1. A schematic illustration showing that a stable structure corresponds to a minimum of internal energy.

When comparing two different structures the energy difference (ΔE) is a measure of their relative stabilities.

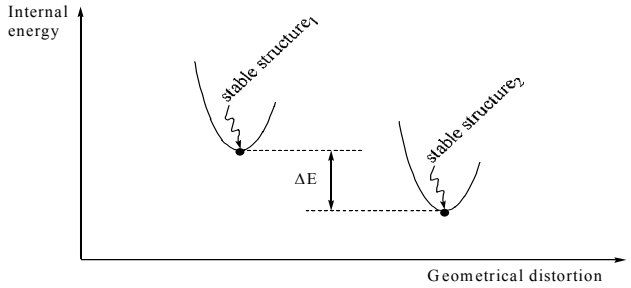


Figure. 1.1.1—2. A schematic illustration showing that the energy differences (ΔE) is a measure of relative stability.

If there is a path between the two minima, i.e. if the system can go from one minima to another, then ΔE is related to the equilibrium constant (K) between the two stable structures

$$\text{stable structure}_1 \underset{}{\overset{K}{\rightleftharpoons}} \text{stable structure}_2$$

1.1.1—1. eq.

If there is a path between the two structures, the geometrical distortion necessary to go from stable structure$_1$ to stable structure$_2$ is called the reaction coordinate. The reaction coordinate measures the reaction's progress from one structure to another. In a one-step reaction the energy rises to a maximum value, then lowers as it passes along the reaction coordinate from the reactant state (R) to the product state (P). The energy maximum between R and P is normally referred to as the transition state and is frequently denoted as TS or ‡. [1] The variation in energy along the reaction coordinate is frequently called the energy profile of the chemical change from reactant to product.

$$R \rightarrow [TS^{\ddagger}] \rightarrow P$$

1.1.1—2. eq.

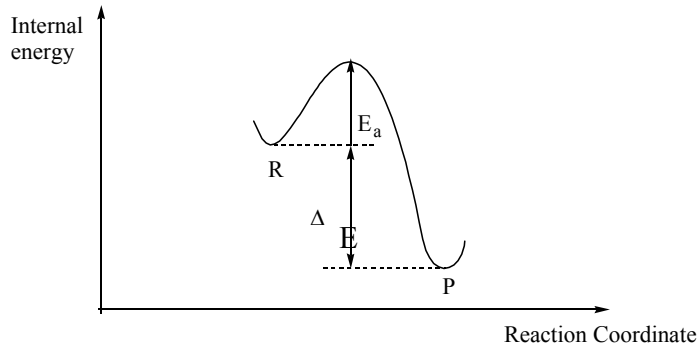


Figure 1.1.1—3. A schematic illustration showing the reaction profile for a one-step reaction.

While ΔE is related to the equilibrium constant (K), the energy of activation (E_a), or the barrier height, predetermines the specific rate (k), or specific velocity of the reaction

$$k = Ae^{-Ea/RT}$$

1.1.1—3. eq

where A is the frequency factor, R is the universal gas constant and T is the absolute temperature.

A reaction intermediate is also an energy minimum. Thus, for an overall reaction there must be two transition states, one proceeding and one following a reaction intermediate (I)

$$R \rightarrow [TS^{\ddagger}_1] \rightarrow I \rightarrow [TS^{\ddagger}_2] \rightarrow P$$

1.1.1—4. eq.

The corresponding reaction profile is shown in Figure 1.1.1—4

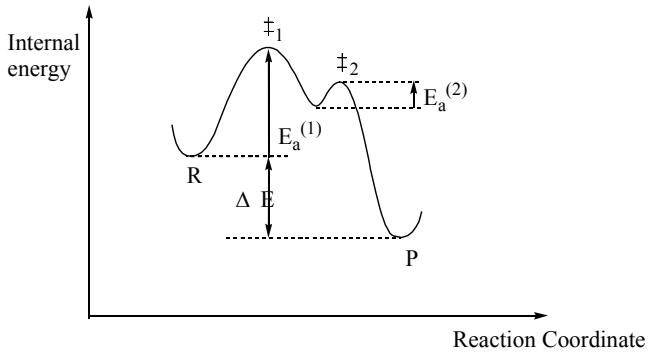


Figure 1.1.1—4. A schematic illustration showing the reaction profile for a two-step reaction.

Usually the first step, characterized by $E_a^{(1)}$, determines the overall rate of the reaction to a good degree of approximation. The possession of this information will enable us to consider the details, the mechanism, of the chemical reaction. Now we can expand on our description of what the purpose of organic chemistry is. The purpose of modern organic chemistry is to study the structure of organic molecules and their reactions as well as the mechanisms involved in converting one organic structure to another.

In order to illustrate this, let us reconsider the reaction presented in the Introduction as shown in 1.1.1—6. eq.:

$$\underset{\text{Bond breaking}}{HO^-+R\text{-}Cl} \longrightarrow \underset{\text{Bond makeing}}{HO\text{-}R+Cl^-}$$

1.1.1—5. eq.

In this reaction, we are breaking one bond and making another bond. In principle, we have two mechanisms, but if the bond breaking and bond making are occurring simultaneously, then we have a one-step or concerted mechanism:

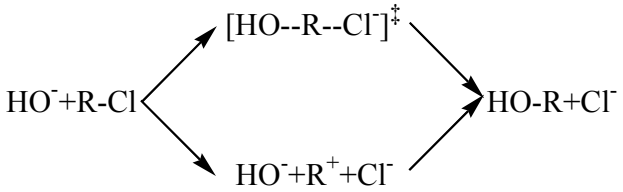
$$HO^-+R\text{-}Cl \longrightarrow [HO\text{--}R\text{--}Cl^-]^{\ddagger} \longrightarrow HO\text{-}R+Cl^-$$

1.1.1—6. eq.

Such a reaction is an example of a substitution (S), i.e. Cl is substituted by HO. Since the reagent $HO^{(-)}$ is negatively charged and, therefore, nucleophilic (N) or “nucleus-loving” and because two (2) molecules (i.e. $HO^{(-)}$ and R-Cl) are involved in the reaction, this reaction path is called an S_N2 mechanism. In this case the reaction profile will look something like the one shown in Figure 1.1.1—3

In contrast to the above, if the bond breaking precedes the bond making, then only one molecule is involved; and therefore this nonsynchronous or stepwise path is called an S_N1 mechanism. In this case, the bond breaking process clearly leads to a stable intermediate; thus, the reaction profile will be like the one shown in Figure 1.1.1—4.

The two mechanisms are shown together in1.1.1—7. eq.:



1.1.1—7. eq.

There are two questions associated with competing mechanisms such as the ones shown in1.1.1—7. eq. First of all "which mechanism will dominate the reaction?" The answer to this question is simple; the mechanism which is faster will dominate the reaction, and the one that has the smallest overall activation energy (E_a), i.e. the lowest barrier height, will be the faster one. The second question is "what makes one barrier lower than the other?" The answer to this question is "the molecular structure". This was hinted at in the Introduction in equation 11 eq. Three molecular structures are given below. In Case I, the S_N2 mechanism dominates. In Case II, a mixture of S_N1 and S_N2 mechanisms occurs side by side and in Case III the S_N1 mechanism dominates.

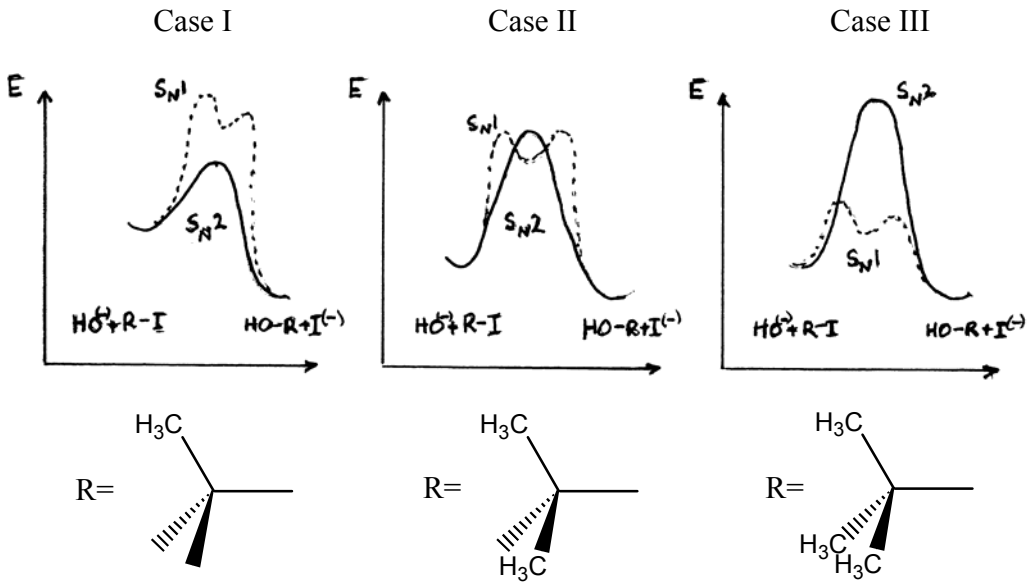


Figure 1.1.1—5. A schematic illustration of how structural change (i.e. a variation in R) can influence the dominating reaction mechanism. [See appendix 1]

1.1.2 Polar and Ionic Structures

Ionic bonds play an extensive role in chemistry. However, the explanation of ionic bond stability is not as straightforward as that of covalent bond stability. Take for instance table salt: NaCl. In its ionic form it consists of two ions: $Na^+ + Cl^-$. This implies that the Na atom is ionized and the Cl atom captures the electron removed in the ionization process. A comparison of the energetics of these two processes, with respect to the atomic state, Na • + • Cl, is shown below in Figure 1.1.2—1:

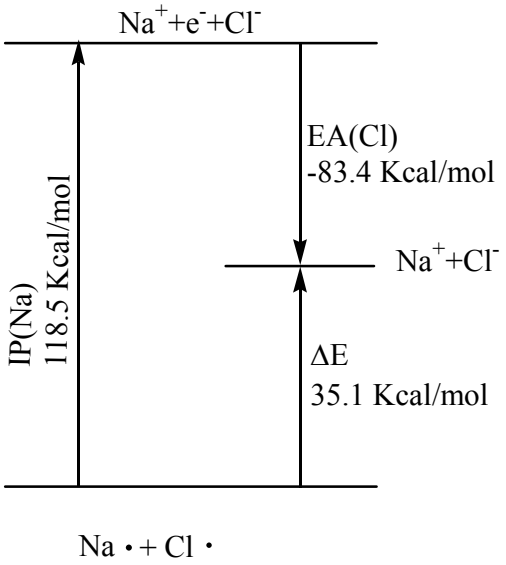


Figure 1.1.2—1. Energetics of electron transfer from the sodium atom to the chlorine atom.

Thus, NaCl would not occur as an ion pair in the gas phase! In fact, Na• and •Cl is a more stable form. However, due to the octet rule, Na and Cl must be covalently bonded to each other in the gas phase as illustrated in Figure 1.1.2—2. Yet, NaCl does exists in the ionic form in a crystal and in solution.

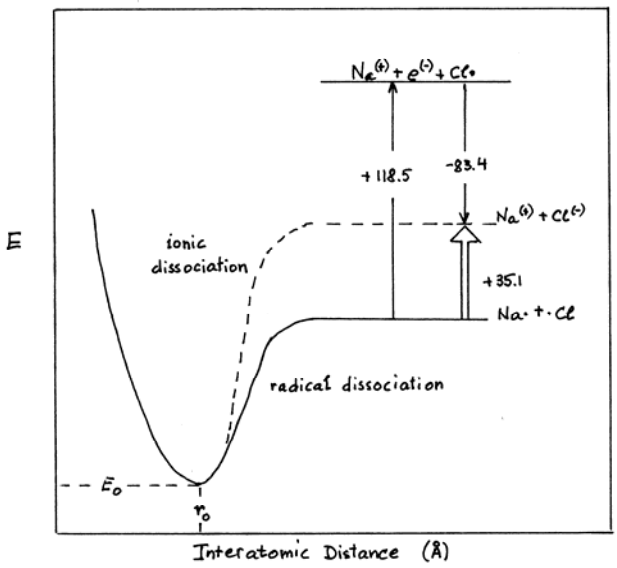


Figure 1.1.2—2. A schematic representation of radical and ionic dissociation (stretching) potentials, for Na—Cl in the gas phase[2].

In a sodium chloride crystal, each Na^+ ion is surrounded by 6 Cl^- ions and each Cl^- ion is surrounded by 6 Na^+ ions. Thus, the ions are stabilized within their environments:

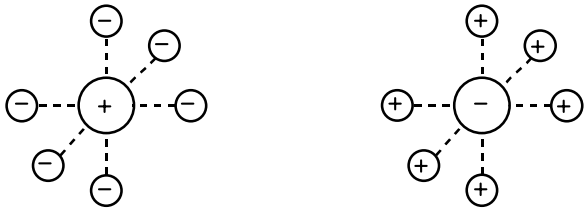


Figure 1.1.2—3. Nearest neighbours for a cation (left) and an anion (right) in sodium chloride crystals.

The ion-ion interaction namely the electrostatic attraction of the + and - ions amounts to -187.86 kcal/mol (i.e., -788 kJ/mol) which easily overcomes the 35.1 kcal/mol endothermicity of ion formation. Thus the ionic crystal will be a stable entity.

In solution, each of the two ions is solvated extensively, amounting to a total of -187.26 kcal/mol (-783.5 kJ/mol)[3] stabilization. In this case, it is not an ion-pair attraction but an ion-dipole interaction, which stabilizes the ions.

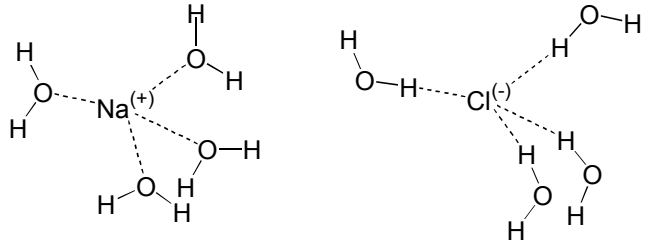
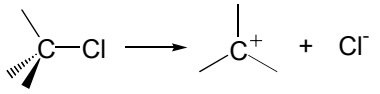


Figure 1.1.2—4. Solvation models for Na^+ and Cl^- ions in aqueous solution (aq). Only four solvent molecules are shown in distorted tetrahedral arrangement for the sake of simplicity.

Consequently, the ionic and covalent dissociation limits of the stretching potentials, given in Figure 1.1.2—5, are reversed, due to the fact that Na• and •Cl are only moderately solvated, while the solvation, and associated stabilization, for the Na^+ and Cl^- ion pair are extensive.

In summary: The existence of ionic chemistry is due to environmental effects (crystal lattice stabilization or stabilization by solvation).

The phenomenon is analogous in organic compounds, but here solvation plays an even more important role. The ion pair formation, via ionic dissociation, of a C — Cl bond (Figure 1.1.2—6)



1.1.2—1. eq.

may be compared to the ionic dissociation of Na — Cl (c.f. Figure 1.1.2—2)

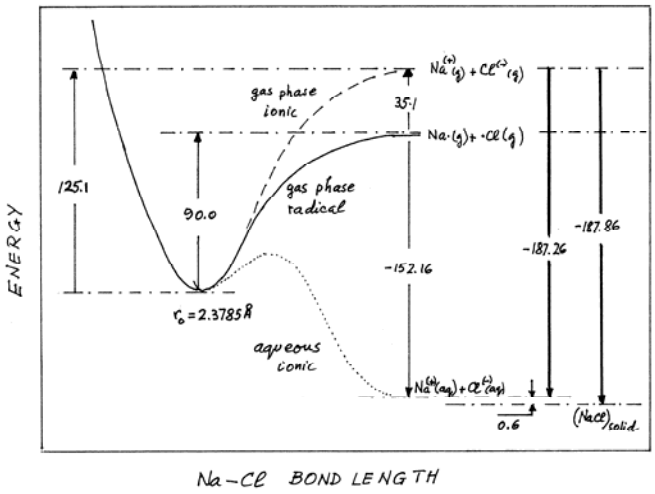


Figure 1.1.2—5. A schematic representation of the stabilizing change of ionic dissociation potential for Na — Cl, on going from the gas phase to aqueous solution. According to the data presented, the ions are stabilized almost to the same extent in solution (only a 0.6 kcal/mol difference) as they are in the crystal lattice. In diatomic NaCl, the separation between Na and Cl atoms is 2.3785 Å, while in the solid crystal it is 2.81 Å.[3]

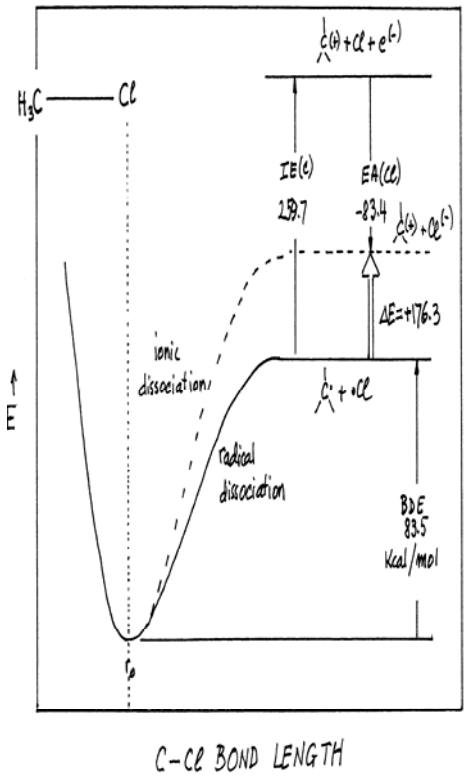


Figure 1.1.2—6. A schematic representation of radical and ionic dissociation (stretching) potentials for the C—Cl bond in the gas phase.

It is obvious from Figure 1.1.2—6 that solvation (c.f. Figure 1.1.2—4) must overcome the 176 kcal/mol energy requirement.

It is clear, therefore, that while most bonds in organic compounds are covalent, the reactions, which are carried out in solution, are in general ionic. It is true that free radical reactions occur once in a while but by and large most organic reactions are ionic in nature. The large stability effect of solvatation makes ionic reactions possible.

However, even if compounds are covalent they are not necessarily apolar. The polarity or ionic character of a bond is predetermined by the electronegativity of the atoms involved in forming the bond. Electronegativity is a measure of the net electron-withdrawing effect of an atom.

Pauling defined electronegativity (EN) as a scaled average or arithmetical mean of ionization potential (IP) and electron affinity (EA), measured in units of eV / particles:

$$EN = f \frac{(IP + EA)}{2}$$

1.1.2—2. eq.

where the scaling factor, f, may be arbitrarily chosen between the following two values[4]:

$$\frac{1}{1.8} \geq f \geq \frac{1}{2.2}$$

1.1.2—3. eq.

Thus, $f \approx ½$. The following table gives the EN values of frequently occurring atoms.

Table 1.1.2-1. Electronegativity values for selected elements of the Periodic Table.

Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8						Br 2.8
			H 2.1			

The ionic character of a bond, as measured by the charge separation $|\delta|$, is related to the electro negativity difference, $\Delta(EN)$, in the following fashion:

$$|\delta| = 1 - e^{-1/4[\Delta(EN)]}$$

1.1.2—4. eq.

This is illustrated in Figure 1.1.2—7

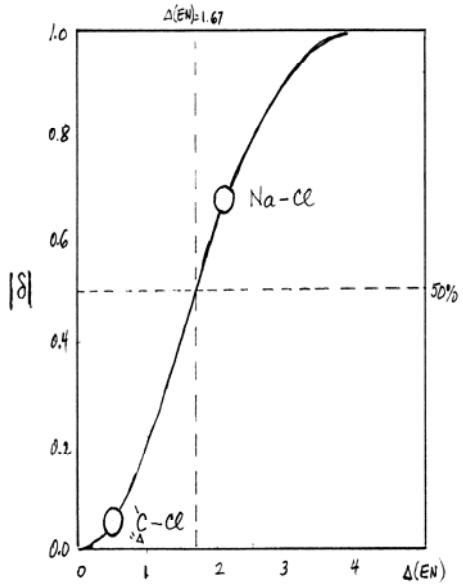


Figure 1.1.2—7. The variation of percentage ionic character or net atomic charge $|\delta|$ of a bond as a function of electronegativity difference (Pauling's equation).

The position of Na — Cl and C — Cl are shown. In the case of NaCl:

$$\Delta\,(EN) = 3.0 - 0.9 = 2.1$$

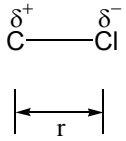
1.1.2—5. eq.

Therefore, the molecule is very ionic (c.f. Figure 1.1.2—7). In the case of a C — Cl bond:

$$\Delta\,(EN) = 3.0 - 2.5 = 0.5$$

1.1.2—6. eq.

Therefore, only a modest charge separation is possible:



1.1.2—7. eq.

This is clearly illustrated in Figure 1.1.2—7. This leads to the concept of dipole moment, the physical measure of bond polarity:

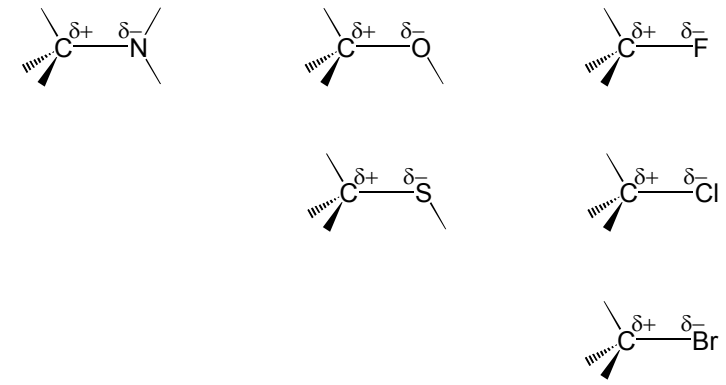
$$\vec{\mu} = |\delta|\vec{r}$$

1.1.2—8. eq.

Note that dipole moment is a vector and by chemical convention it points from the + pole to the - pole (in the physicists' convention it points from - to +).[See appendix 3] Most

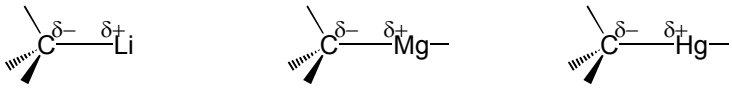
organic reactions are ionic, and 'ionic' frequently means bond dissociation to ion pairs. Clearly a bond which is already polar will undergo ionic dissociation with greater ease than a nonpolar bond, because a polarized bond is tending towards ionic dissociation. But the extent of bond polarization is predetermined by the difference between electronegativities, Δ(EN), of the atoms that constitute the bond. For this reason, the data presented in Table 1.1.2-1 is of upmost importance. Many properties of organic functional groups can, not only be understood, but in fact, be predicted from the Δ(EN) values.

Note that elements from the upper right hand side of the periodic table have larger electronegativity values than carbon. Consequently, for bonds incorporating such elements, carbon will be electropositive. (See appendix exercise 3)



1.1.2—9. eq.

In contrast to the above, in a carbon-metal bond the electronegativity of the carbon is larger; therefore, the bond polarization is such that the carbon will carry excess negative charge.



1.1.2—10. eq.

Clearly, carbon in the first class, 1.1.2-9, will react cationically as an electrophile (like a Lewis acid), while carbon in the second class, 1.1.2-10, will react anionically as a nucleophile (like a Lewis base).

Intramolecular Interactions

Interactions between molecules are important for several reasons. One example is the interaction between the solvent and solute as shown in Figure 1.1.2—4. Such interactions play a key role for certain reactions, which occur in a given polar solvent, but do not take place in apolar solvent. Intermolecular interactions are also important because reactants and reagents can also form complexes, either with themselves or with catalysts prior to the reaction.

The interaction energy depends greatly on the types of species interacting. The largest energy is that of the ion-ion interaction; it can be repulsive, in the case of like charges, or attractive, in the case of opposite charges. The ion-ion energy of interaction may be as large

as 400 kcal/mol. Covalent bond formation is governed by energy lowering, within the range of 30 - 150 kcal/mol depending on the atoms involved. O - O bond formation releases about 50 kcal/mol while the I - I bond gives about 36 kcal/mol. At the other extreme of the scale, we find BDE values higher than 100 kcal/mol. For example, H - H: 104 ; H - O : 119 ; H - F : 136 ; B - F : 150 kcal/mol.5 However, the BDE for a single bond that contains a carbon is usually not larger than 120 kcal/mol. Multiple bonds are stronger.

Of the weaker interactions we should consider ion-dipole, dipole-dipole, hydrogen bond and van der Waals interactions. All of these are summarized in Figure. Although these interaction energies can now be calculated quite accurately by ab initio quantum chemistry, the mathematical models (c.f. Figure1.1.2-8) developed earlier are still quite useful.

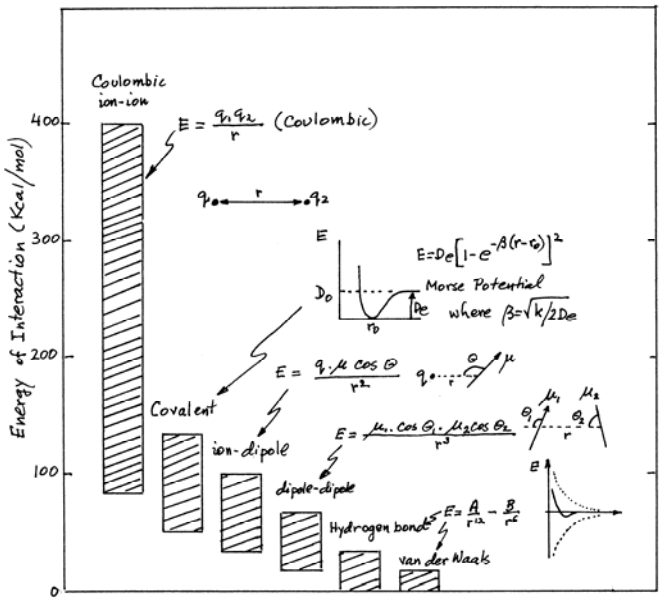


Figure 1.1.2—8. A schematic illustration of the approximate energy range for various intermolecular interactions (shaded bars at the lower left-hand side). Physical models and their mathematical expressions for the various intermolecular interactions are depicted at the upper right hand side of the figure.

The following chemical structures are given to illustrate the ion-dipole, dipole-dipole and hydrogen bond interactions:

1.1.2—11. eq.

(ion-dipole)

1.1.2—12. eq.

(dipole-dipole)

1.1.2—13. eq.

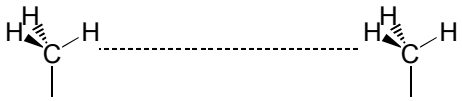
(hydrogen bond)

The Van der Waals interaction may involve two groups of closed electronic shells, for example two Ne atoms:

Ne ····· Ne

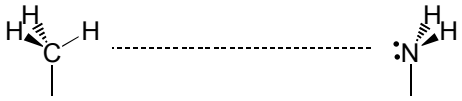
1.1.2—14. eq.

The interaction between two alkyl groups 1.1.2—15. eq. is probably not very energetically stable. The addition of a heteroatom to one of the two groups increases the stability of the interaction.



1.1.2—15. eq.

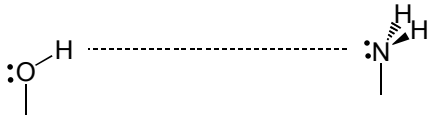
The two interactions depicted in 1.1.2—16. eq. traditionally are not considered to be hydrogen bonding because the H atoms attached to carbon are not very protic. However more recently such interactions, involving C-H protons are classified as very week interactions.



1.1.2—16. eq.

1.1.2—17. eq.

Nevertheless, the interaction specified in 1.1.2—18. eq. is a genuinely hydrogen-bonded system:



1.1.2—18. eq.

Some of the mathematical models given in Figure1.1.2-8, together with other formulas not shown on figure, can be combined to compute internal potential energies. The equations may be combined in a number of possible ways. The combined equations, collectively referred to as “force - fields”, incorporate a large number of empirical parameters which depend on the types of atoms involved, as well as their states of hybridization (structural motifs). These force-field methods are used currently in organic chemistry, biochemistry, pharmacology, etc., for Molecular Mechanics (MM) and Molecular Dynamics (MD) simulations. Such molecular modelling computer packages are commercially available for personal computers (PC), workstations or supercomputers. The molecules, which we discuss in an Introductory Organic Chemistry course, can in fact, be studied by molecular modelling programs on a PC.

Acids, bases and their complexes

We can distinguish between two types of bases and two types of acids based on two classification systems for acids and bases. One definition, which was offered by the Danish chemist Johannes Bronsted in 1923, and independently by the English chemist Thomas Lowry, is referred to as the Bronsted - Lowry theory of acids and bases.

The other definition of acids and bases was offered by the famous American chemist Gilbert N. Lewis as a consequence of his dot-pair model of bonding. His theory of electron pair bonding in 1916 predates the discovery of Quantum Mechanics (1926) by a decade. The Lewis acid/base definition is based on an electron pair acceptor/electron pair donor concept, while the Bronsted definition is based on proton donation/proton acceptance.

Table 1.1.2-2. Bronsted and Lewis classification of acids and bases in terms of their acceptance or donation of protons or electron pairs.

	Bronsted	Lewis
Acid	Proton donor	Electron pair acceptor
Base	Proton acceptor	Electron pair donor

A Lewis acid-base reaction produces a Lewis complex:

$$B: {}^{(-)}+{}^{(+)}A \rightarrow B \rightarrow A$$

1.1.2—19. eq.

$$Me_3N: + BF_3 \rightarrow Me_3N \rightarrow BF_3$$

1.1.2—20. eq.

Lewis Base Lewis Acid Lewis Complex

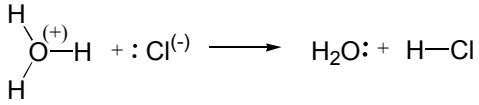
1.1.2—21. eq.

The arrow on the bonds in 1.1.2—19. eq. and 1.1.2—20. eq. denotes a “dative bond” which implies that both electrons of the electron pair originate from one of the two components. Equation 1.1.2—12. eq. is also an example of the formation of a Lewis complex.

A Bronsted acid-base reaction produces another acid-base pair:

$$B_1 : H+ :B_2^{(-)} \rightarrow B_1:^{(-)} + H—B_2$$

1.1.2—22. eq.



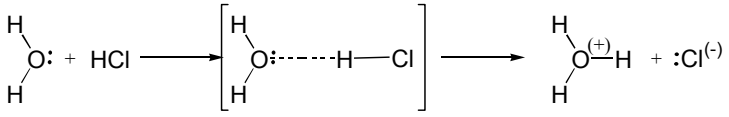
Bronsted Acid | Bronsted Base | Bronsted Base | Bronsted Acid

1.1.2—23. eq.

Equations 1.1.2-22 and 1.1.2-23 also exemplify a Bronsted acid-base reaction.

[For computational exaple see Apprendix 4.]

There is, however, an opportunity for complex formation between a Bronsted acid and a Bronsted base as exemplified below for the H_2O + HCl system. This Bronsted complex is usually referred to as a hydrogen bonded (HB) complex:



Bronsted Base | Bronsted Acid | Bronsted or H-bonded Complex | Bronsted Acid | Bronsted Base

1.1.2—24. eq.

The energy profiles for the two types of acid-base reactions in the gas phase are shown in Figure 1.1.2—9

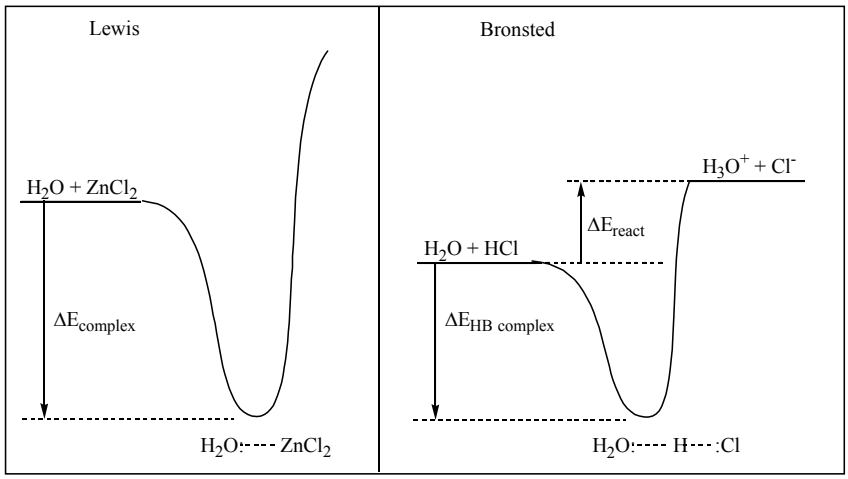


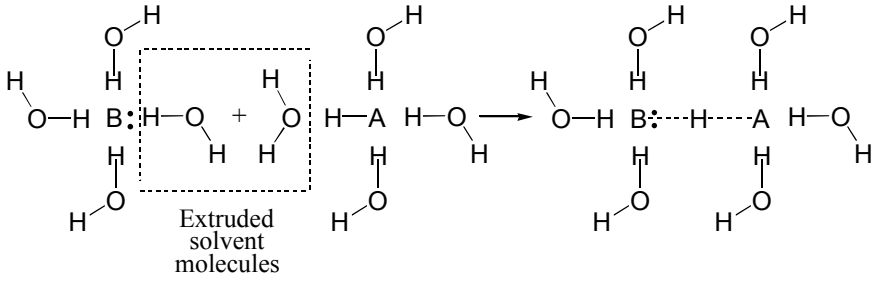
Figure 1.1.2—9. Schematic energy profiles for Lewis and Bronsted acid-base reactions

Note that the stabilization energy by solvation is greatest for the ion pair, intermediate for the neutral pair, and smallest for the hydrogen bonded (HB) Bronsted complex:

$$\left|\Delta E_{solvation}\,[H_3O^{(+)} + Cl^{(-)}]\right| > \left|\Delta E_{solvation}[H_2O + HCl]\right| > \left|\Delta E_{solvation}[H_2O\ldots H\ldots Cl]\right|$$

1.1.2—25. eq.

In the neutral pair both components are solvated but when the complex is formed some solvent molecules are extruded from the in-between region. Consequently, the complex is stabilized to a lesser extent than the neutral components.



1.1.2—26. eq.

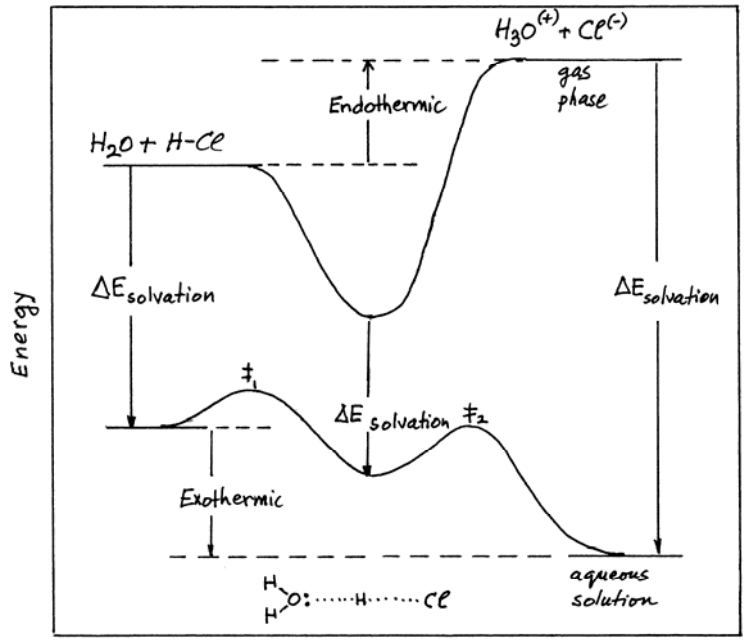
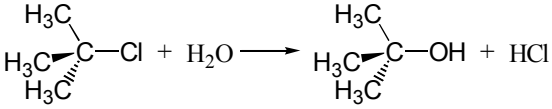


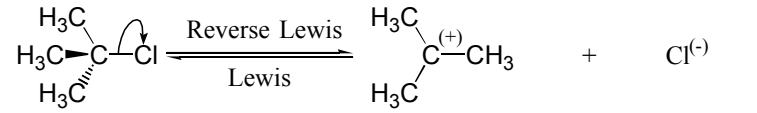
Figure 1.1.2—10. A schematic illustration of solvent effect on a Bronsted acid-base reaction.. (H_2O + HCl is used only to exemplify the proton transfer.) (See appendix 5)

The two barriers, denoted by ‡ in the lower part of Figure 1.1.2—10, measure the energy requirement for the rearrangements of the solvation shell. (For $\ddagger_2$ this is illustrated by 1.1.2—26. eq.). In agreement with the acid-base reactions presented in 1.1.2—19. eq., 1.1.2—20. eq. and 1.1.2—22. eq. - 1.1.2—24. eq., one may infer, from the mechanistic equations presented earlier that organic chemistry is nothing more than an exercise in acid-base chemistry. Clearly, both the Lewis and Bronsted acid-base concepts play an important role in understanding organic reaction mechanisms! Take for example the S_N1 mechanism for the following reaction:



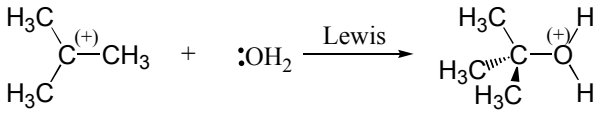
1.1.2—27. eq.

All the individual steps of the mechanism may be analysed in terms of either Lewis or Bronsted acid-base reactions.



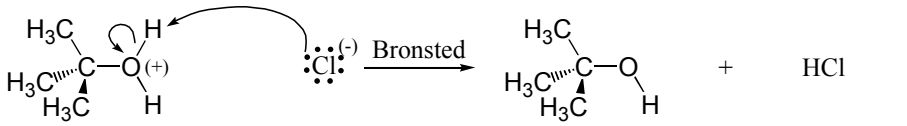
Lewis complex Lewis acid Lewis base

1.1.2—28. eq.



Lewis acid Lewis base Lewis complex

1.1.2—29. eq.



Bronsted acid Bronsted base Bronsted base Bronsted acid

1.1.2—30. eq.

Since acidity and basicity are so important, we need to spend some time in solidifying our understanding of acid strength and base strength.

1.1.3 Fundamentals of Thermodynamics and Kinetics

Both thermodynamics and kinetics are important in the elucidation of reaction mechanisms. The area of investigation of these two topics is illustrated by the figure below.

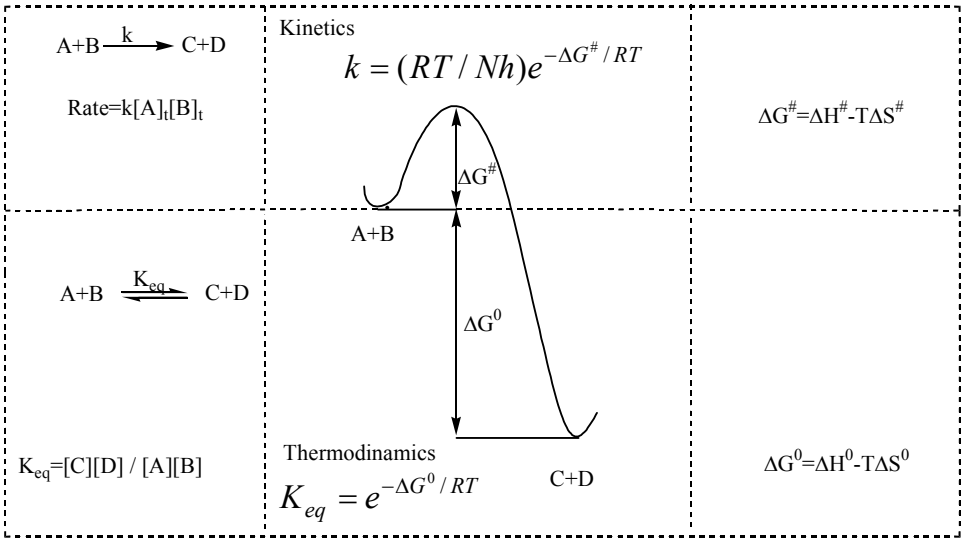
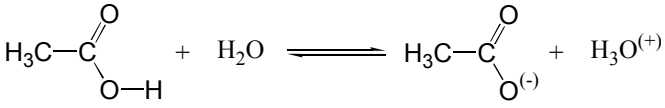


Figure1.1.3—1. A schematic illustration of the effective domain of thermodynamics and kinetics in studying chemical reactions.

Since not all reactions reach the equbrium we shall illustrate the thermodynamics of reactions via the ionization of acids, which almost always reach equilibrium within a short time.

The thermodynamics of equilibria

As may be inferred from Figure 1.1.2—10, proton transfer reactions are very fast because the energy barriers (‡$_1$ and ‡$_2$) along the reaction coordinates are very small. Consequently, proton transfer equilibrium is established almost immediately.



1.1.3—1. eq.

$$K_{eq} = \frac{[CH_3COO^{(-)}]\,[H_3O^{(+)}]}{[CH_3COOH]\,[H_2O]}$$

1.1.3—2. eq.

As 1.1.3—1. eq. indicates, the equilibrium in this case is shifted to the left; thus, less than 50% of acetic acid is dissociated in aqueous solution. The energetics of the process certainly predetermines the position of the equilibrium and, therefore, the equilibrium constant K_{eq}. For this reason, a review of the basic principles of thermodynamics (usually taught, but seldom learned in first year chemistry courses) is in order.

There are two ways to carry out an experiment, at constant pressure or at constant volume. Most of our experiments are done in open vessels and the atmospheric pressure is usually constant during the experiment. For a constant volume experiment, we need a sealed

piece of equipment usually referred to as an autoclave, like a pressure cooker. The two modes of measurements, constant volume and constant pressure, yield slightly different results and we need to give different names to these thermodynamic functions.

At constant volume, the observed heat of the reaction corresponds to the energy change (ΔE) and at constant pressure the heat of the reaction corresponds to the enthalpy change (ΔH). These two quantities do not differ from each other by very much; fundamentally the difference is due to $\Delta(PV)$. Sometimes the difference is only RT which amounts to 0.6 kcal/mol at 300K. However, the distinction between ΔE and ΔH is important. Since most of our experiments are carried out at constant pressure, ΔH is quoted more often than ΔE. We might mention, in passing, that in Quantum Chemistry, ΔE needs to be augmented by a correction term to obtain ΔH.

Thermal energy or enthalpy cannot freely be converted to work. In other words, the conversion efficiency can never be 100%! The reason for this is due to the fact that thermal energy and enthalpy are partially disordered and only the ordered portion can be converted to work. The extent of disorder is proportional to the absolute temperature, T(K), and the proportionality constant is called the entropy change: ΔS

$$\text{Extent of disorder} = T\Delta S$$

1.1.3—3. eq.

This quantity, the extent of disorder, is the same for the energy and the enthalpy change. Consequently, the portion of the energy, which is freely convertible to work, the “free energy” or “Helmholz free energy”, corresponds to the following difference (Volume = const.):

$$\Delta A = \Delta E - T\Delta S$$

1.1.3—4. eq.

One may write a similar difference for the enthalpy (Pressure = const):

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

1.1.3—5. eq.

This quantity (ΔG) denotes “free enthalpy”, but it is usually referred to as “Gibbs free energy” in honour of the great thermodynamicist Josiah W. Gibbs (1839-1903) who was professor at Yale from 1869 until 1903.

The equilibrium constant K_{eq}, such as the one given in 1.1.3-2 for the ionization of an acid, is related to $\Delta G°$ according to 1.1.3-7. Note that superscript ° in $\Delta G°$ implies standard Gibbs free energy at 1 atm pressure for gases and 1M concentration for solutions.

$$K_{eq} = e^{-\Delta G°/RT}$$

1.1.3—6. eq.

$$\Delta G° = -2.303RT \log K_{eq}$$
$$\text{or } \Delta G° = -RT \ln K_{eq}$$

1.1.3—7. eq.

where R = 1.987 cal/mol ≈ 0.002 kcal/mol/K and T is the absolute temperature in Kelvin units; [i.e., T(K) = 273.2 + t (°C)]. This equation clearly shows that the driving force for any reaction is ΔG°. If ΔG°<< 0 the reaction is driven to the right (K_{eq} >> 1); if ΔG°>> 0 then K_{eq} << 1, and if ΔG°=0 then K_{eq}=1.0. [For further exercise see appendix 5]

Acid and Base Strengths as measured indirectly by K_{eq}

No matter how important equilibrium constants are, acid strengths are not measured directly by their K_{eq} value. The K_{eq} value represents the full equilibrium constant as in 1.1.3—2. eq.or in 1.1.3—8. eq. and 1.1.3—9. eq.:

$$H_2O + HA \xrightleftharpoons{K_{eq}} H_3O^{(+)} + A^{(-)}$$

1.1.3—8. eq.

$$K_{eq} = \frac{[H_3O^{(+)}]\,[A^{(-)}]}{[H_2O]\,[HA]}$$

1.1.3—9. eq.

but acid strength is measured by a pseudo equilibrium constant, K_a, from which the water concentration is omitted 1.1.3—10. eq.and 1.1.3—11. eq.:

$$HA \xrightleftharpoons{K_a} H^{(+)} + A^{(-)}$$

1.1.3—10. eq.

$$K_a = \frac{[H^{(+)}]\,[A^{(-)}]}{[HA]}$$

1.1.3—11. eq.

Clearly, the two constants are related to each other according to 1.1.3—12. eq.:

$$K_a = K_{eq}\,[H_2O]$$

1.1.3—12. eq.

For historical reasons, acid strength has been expressed as the negative log of base 10 of K_a. This quantity is denoted as pK_a (the power of K_a)

$$pK_a = -\log K_a$$

1.1.3—13. eq.

Now if we wish to relate ΔG° to pK_a, we must take -log of equation 1.1.3—12. eq.and rearrange it. The result of this elementary manipulation is given in 1.1.3—14. eq.

$$\Delta G° = 2.303RT \{pK_a + \log [H_2O]\}$$

1.1.3—14. eq.

Knowing that RT = 0.002 x 300 = 0.6 and $[H_2O]$ = 55.56 M, thus, log $[H_2O]$ = 1.745, we obtain 1.1.3—14. eq. in a numerical form.

$$\Delta G° = 1.3818 \{pK_a + 1.745\}$$

1.1.3—15. eq.

(See appendix exercise 6) Note that ΔG° = 0 does not occur at pK_a = 0. Instead if ΔG° = 0 then

$$pK_a = - \log [H_2O] = -1.745$$

1.1.3—16. eq.

The relationships between ΔG°, K_{eq}, K_a and pK_a are summarized in Figure1.1.3-2:

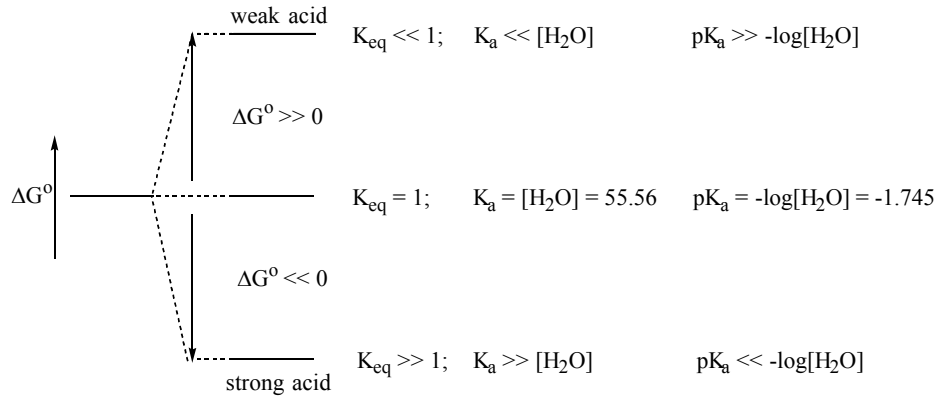


Figure 1.1.3—2. Three extreme cases for acid strengths.

The relationships between structure and acidity are summarized below. The acidity increases with the electronegativity of the atom that carries the H:

$$C—H < N—H < O—H < F—H$$

1.1.3—17. eq.

Acidity increases as we descend a vertical column of the periodic table:

$$HF < HCl < HBr < HI$$

1.1.3—18. eq.

Acidity decreases with increasing hybridization:

$$sp > sp^2 > sp^3$$

1.1.3—19. eq.

Thus we may note the follow in three pKa values: C_2H_2 is 25, C_2H_4 is 44 and C_2H_6 is 50.[6] Acidity increases with the inductive, i.e., more electron withdrawing, effect of the substituent:

$$FCH_2–COOH > ClCH_2–COOH > BrCH_2–COOH$$

1.1.3—20. eq.

Acidity increases with the number of electron withdrawing groups (EWG):

$$F_3C–COOH > F_2HC–COOH > FH_2C–COOH > H_3C–COOH$$

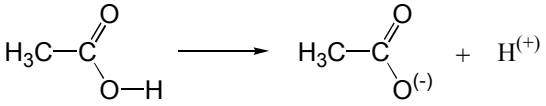
1.1.3—21. eq.

Acidity increases with increasing resonance in the conjugate base:

$$R–COOH \ > \ R–CH_2–OH$$

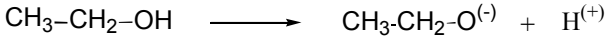
1.1.3—22. eq.

Even though, pK_a is defined as a measure of acid strength it can also be used to measure the strength of its conjugate base.



$pK_a = 4.75$

1.1.3—23. eq.



$pK_a = 16$

1.1.3—24. eq.

Thus, acetic acid is a stronger acid than ethyl alcohol but the acetate ion is a weaker base than the ethoxide ion. Thus the larger the pK_a value of the conjugate acid, the stronger the base will be the following set of equations illustrates this point for three families of compounds.

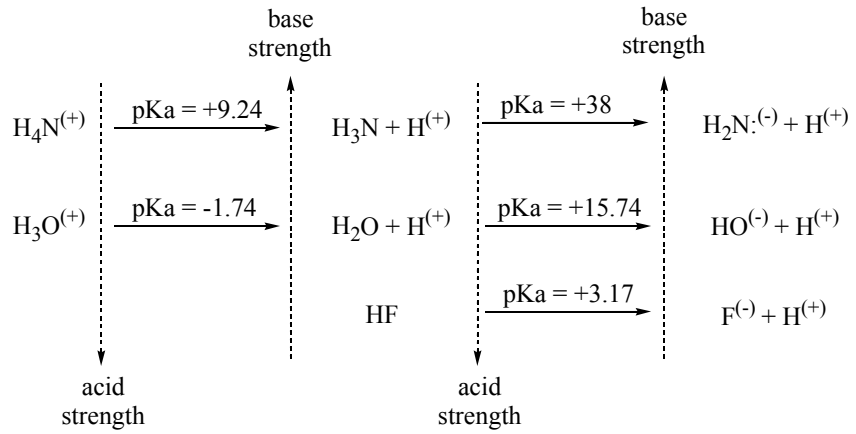


Figure 1.1.3—3. Inorganic superacids and weak organic acids.

Starting with the definition of pK_a (c.f. 1.1.3—8. eq. and 1.1.3—10. eq.)

$$HA \underset{}{\overset{K_a}{\rightleftharpoons}} H^{(+)} + A^{(-)}$$

1.1.3—25. eq.

$$K_a = \frac{[H^{(+)}]\,[A^{(-)}]}{[HA]}$$

1.1.3—26. eq.

$$pK_a = pH - \log \frac{[A^{(-)}]}{[HA]}$$

1.1.3—27. eq.

when half ionization is achieved,

$$[HA] = [A^{(-)}]$$

1.1.3—28. eq.

the pH of the solution measures the acid strength of the solute:

$$pK_a = pH$$

1.1.3—29. eq.

The pH scale is defined from 0 (1M HCl) to 14 (1M NaOH) though stronger acids produce solutions which are more acidic than pH = 0. But the acidity of these solutions would require a negative pH, so the pH scale is restricted to a range of 0 to 14. These negative values are characterized by an ‘acidity function’ and denoted by H_0. Stronger bases would yield a pH > 14, the symbol H_- is used to denote the basicity of these solutions.

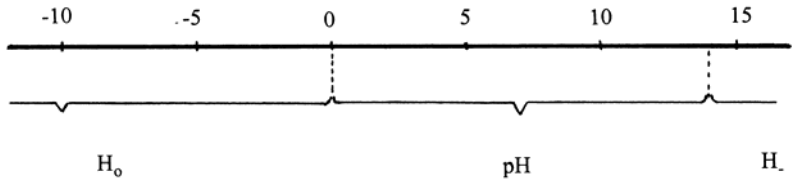


Figure 1.1.3—4. The extension of the pH scale.

Very strong acids have negative pK_a values and therefore produce solutions with $H_0 << 0$. This is true even for concentrated sulfuric acid. However acids, stronger than 100% sulfuric acid, may be produced when a Bronsted acid is mixed with a Lewis acid. These are called superacids. The most commonly occurring superacid is fuming sulfuric acid which is a mixture of H_2SO_4 and SO_3. Some examples are listed in the table below with H_0 values ranging from -11 to -30.[7]

Table 1.1.3-1 Acidity of superacids

Superacid	[Lewis Acid] %	$-H_0$
$H_2SO_4 + SO_3$	50	12 - 14.5
$H_2SO_4 + B(OSO_3H)_3$	30	12 - 14.0
$(SO_3)H^+ + SbF_6^-$	90	15 - 26.5
$CF_3 - SO_2 - OH + SbF_5$	10	14 - 18
$HF + SbF_5$	2	11 - 20
$HF + SbF_5$	50	20 - 30
$HF + TaF_5$	0.6	11 - 19
$HF + BF_3$	7	11 - 7

While very strong acids have negative pK_a values, most organic acids are weak acids or extremely weak acids.

It should be noted that pK_a values which are smaller than 0 and larger than 14 may not be very accurate. For organic acids the following order of acidity may be set up:

$$RSO_2OH > RCOOH > ArSH > ArOH > RSH > ROH > RH$$

1.1.3—30. eq.

Alcohols are to be regarded as very weak acids, since their pK_a values are greater than 14.

Carboxylic acids are the most common organic acids even though they are not the strongest. They are all weak acids having positive pK_a values. However, their actual value can be influenced by substitution as illustrated in Table 1.1.2-2

Table 1.1.3-2. The role of substituent inductive effects on the pKa values of organic acids.

Acid	pK_a	Acid	pK_a
HCOOH	3.77	$HOCH_2COOH$	3.83
CH_3COOH	4.76	CH_3OCH_2COOH	3.53
CH_3CH_2COOH	4.88	$(CH_3)_3N^+CH_2COOH$	1.83
$(CH_3)_2CHCOOH$	4.86	O_2NCH_2COOH	1.68
$(CH_3)_3CCOOH$	5.05	$NCCH_2COOH$	2.47
$CH_2=CHCH_2COOH$	4.35	$Cl_2CHCOOH$	1.29
$PhCH_2COOH$	4.31	Cl_3CCOOH	0.65
FCH_2COOH	2.66	F_3CCOOH	0.23
$ClCH_2COOH$	2.86	$CH_3CH_2CHClCOOH$	2.84
$BrCH_2COOH$	2.86	$CH_3CHClCH_2COOH$	4.06
ICH_2COOH	3.12	$ClCH_2CH_2COOH$	4.52

Of all organic acids, hydrocarbons (RH), are the weakest, as shown in table 1.1.3-2. This is because the C—H bond is not very likely to give up a proton in an ionization process.

For example the pK_a value of ethane is 50[8]

$$CH_3\text{-}CH_2\text{-}H \overset{K_a}{\rightleftharpoons} CH_3\text{-}CH_2{:}^{(-)} + H^{(+)}$$

1.1.3—31. eq.

which makes ethane perhaps the weakest acid known.

Kinetics and mechanism of simple reactions.

The mechanism of a reaction involves the movement of and interactions between atoms and electrons in a reaction. Since reactions occur in time, the details of a reaction become apparent over a certain amount of time. The method that allows us to determine the details of a reaction over time is reaction kinetics. We must investigate the kinetics of a reaction in order to elucidate its mechanism.

First order reactions

In a kinetic study, we measure concentration as a function of time. The concentration profiles obtained for a unimolecular reaction:

$$A \longrightarrow X$$

1.1.3—32. eq.

are given in Figure 1.1.3—5

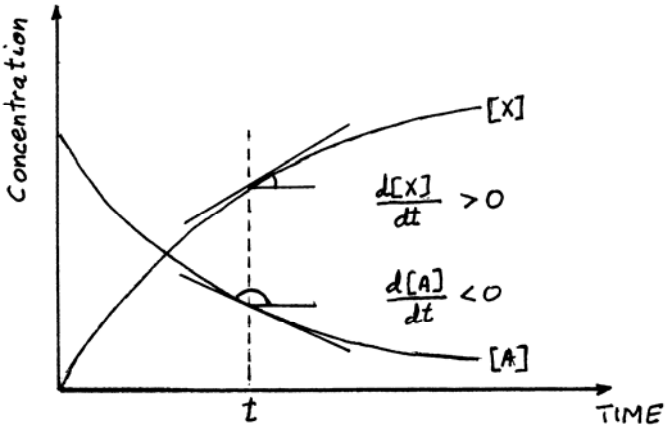


Figure 1.1.3—5.Defining the rate for a chemical reaction (A→X) in terms of concentration-time derivatives. [See appendix 6]

The velocity or the rate of the reaction (v) can be defined in terms of the first derivative of the concentration of product (X) formed over time or the first derivative of the concentration of reactant (A) consumed over time. It is clear from Figure 1.1.3-5 that the absolute values of these two concentration - time derivatives are the same; however, their signs are different (one is the rate of production, the other is the rate of consumption). Thus the rate or velocity (v) of the reaction is defined according to 1.1.3—33. eq.

$$\text{Rate} = v = -\frac{d[A]}{dt} = \frac{d[X]}{dt} = k[A]$$

1.1.3—33. eq.

The right hand side of the equation is a manifestation of the law of mass action since the instantaneous velocity of the reaction is proportional to the instantaneous concentration of the reactant, i.e. [A]. The proportionality constant, k, is called the rate constant or specific rate (the term specific rate implies that v = k, if [A] = 1).

The rate constant is the measure of reactivity. So when we say that an organic compound A is more reactive than an organic compound B, then A has a larger rate constant than B under the same experimental conditions.

$$A \xrightarrow{k_A} X$$

1.1.3—34. eq.

$$B \xrightarrow{k_B} Y$$

1.1.3—35. eq.

$$k_A > k_B$$

1.1.3—36. eq.

If equation 1.1.3—33. eq. is written in its simplest form such as 1.1.3—34. eq.:

$$\frac{d[A]}{dt} = -k[A]$$

1.1.3—37. eq.

then it becomes clear that this is nothing more than a differential equation. Hence, in reaction kinetics, 1.1.3—33. eq. is referred to as the differential rate law. After integrating 1.1.3—34. eq., the equation is referred to as an integrated rate equation, which may be written in a logarithmic 1.1.3—38. eq.or an exponential 1.1.3—39. eq. form, where $[A]_0$ is the initial concentration of A

$$\ln[A] = -kt + \ln[A]_0$$

1.1.3—38. eq.

$$[A] = [A]_0 e^{-kt}$$

1.1.3—39. eq.

This is the general form of a first-order reaction. The rate constant (k) can be determined from 1.1.3—38. eq. since 1.1.3—38. eq. has the form of a straight line (y = mx + b). This is illustrated in Figure 1.1.3—6.

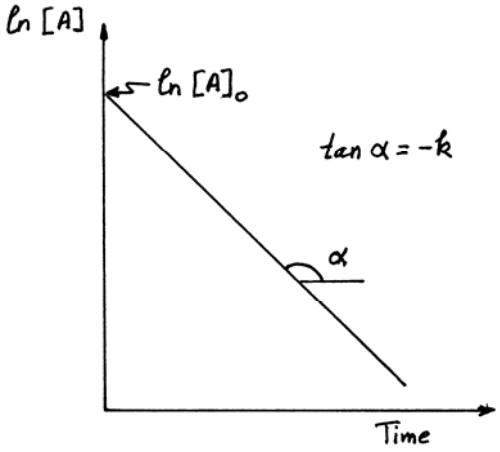


Figure 1.1.3—6. Graphical determination of the first-order rate constant ($\alpha > 90°$, and so $\tan \alpha < 0$)

The reaction rate can be characterized not only by its rate constant but its half-life as well. The half-life (denoted as τ or $t_{1/2}$) of a reaction is the time necessary to reduce the initial reactant concentration to half of its original value:

$$[A] = \frac{1}{2}[A]_0 \qquad \text{at} \qquad t = \tau$$

1.1.3—40. eq.

By substituting 1.1.3—40. eq. into 1.1.3—38. eq., one finds that for a first order reaction the half-life is independent of the initial concentration:

$$\tau = \frac{\ln 2}{k} = \frac{0.693}{k}$$

1.1.3—41. eq.

Second order reactions

A bimolecular reaction 1.1.3—42. eq. is governed by a second order rate law 1.1.3—43. eq.

$$A + B \longrightarrow X$$

1.1.3—42. eq.

$$\frac{d[X]}{d[t]} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]$$

1.1.3—43. eq.

By recognizing, certain equalities associated with mass balance:

$$[A] = [A]_0 - [X]$$

1.1.3—44. eq.

$$[B] = [B]_0 - [X]$$

1.1.3—45. eq.

where $[A]_0$ and $[B]_0$ are the initial concentration of A and B, 1.1.3—43. eq. can be rewritten as 1.1.3—46. eq..

$$\frac{d[X]}{dt} = k\{[A]_0 - [X]\}\{[B]_0 - [X]\}$$

1.1.3—46. eq.

This is the differential rate equation for a second order reaction. Its integrated form, the integrated rate equation, may be written with the explicit inclusion of [X] as 1.1.3—46. eq., or after substituting 1.1.3—44. eq. and 1.1.3—45. eq., without [X] as 1.1.3—47. eq.

$$\frac{1}{[B]_0 - [A]_0}\left\{\ln\frac{[B]_0 - [X]}{[A]_0 - [X]} - \ln\frac{[B]_0}{[A]_0}\right\} = kt$$

1.1.3—47. eq.

$$\frac{1}{[B]_0 - [A]_0}\left\{\ln\frac{[B]}{[A]} - \ln\frac{[B]_0}{[A]_0}\right\} = kt$$

1.1.3—48. eq.

$$\frac{1}{[B]_0 - [A]_0}\ln\frac{[B]}{[A]} = kt + \frac{1}{[B]_0 - [A]_0}\ln\frac{[B]_0}{[A]_0}$$

1.1.3—49. eq.

The latter equation 1.1.3—48. eq.has the form of a straight line (y = mx + b) and may be plotted to determine k as the slope of the plot (c.fFigure 1.1.3—7).

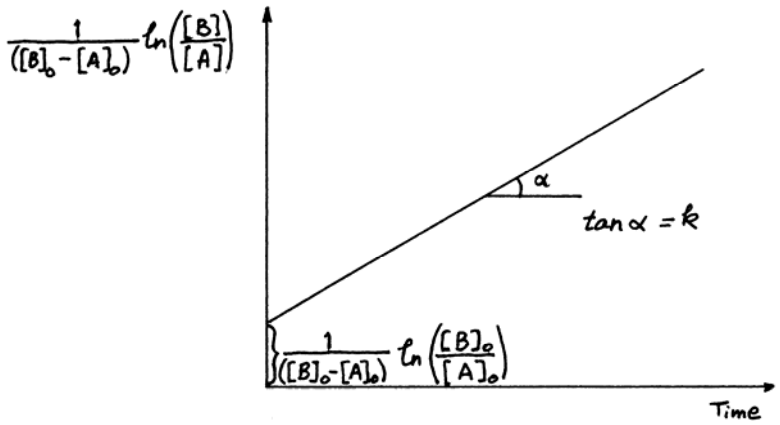


Figure 1.1.3—7. Graphical determination of the second-order rate constant for the v = k[A][B] differential equation ($[A]_0 \neq [B]_0$).

Clearly, equation 1.1.3—48. eq. can only be used if the initial concentrations are not equal. If they are equal, then the denominator will vanish since $[B]_0 - [A]_0 = 0$.

In addition to first and second order reactions, there is also a zero order reaction. These are summarized inTable 1.1.3-3.

Table 1.1.3-3. Rate equations and their characteristics for reactions of various order

Order	Differential rate equation	Integrated rate equation	Half-life time τ	Units of k
0	$-\frac{d[A]}{dt} = k$	$[A]_0 - [A] = kt$	$\tau = \frac{[A]_0}{2k}$	Ms
1	$-\frac{d[A]}{dt} = k[A]$	$\ln[A]_0 - \ln[A] = kt$	$\tau = \frac{\ln 2}{k}$	s^{-1}
2	$-\frac{d[A]}{dt} = k[A]^2$	$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$	$\tau = \frac{1}{k[A]_0}$	$M^{-1}s^{-1}$
	$-\frac{d[A]}{dt} = k[A][B]$	$\frac{1}{[B]_0 - [A]_0}\left\{\ln\frac{[B]}{[A]} - \ln\frac{[B]_0}{[A]_0}\right\} = kt$		

Higher order reactions (i.e., 3, 4, ….. n) are not included in Table 1.1.3-2. If further clarification is needed, students can consult textbooks of Physical Chemistry or Physical Organic Chemistry.

Temperature dependence of k, and activation parameters

Arrhenius's relationship, which was presented earlier in 1.1.1—3. eq., is given here in both its logarithmic and exponential forms in terms of the pre-exponential factor (A) and the energy of activation (E_a).

$$\ln(k) = -\left(\frac{E_a}{R}\right)\frac{1}{T} + \ln(A)$$

1.1.3—50. eq.

$$k = Ae^{-Ea/RT}$$

1.1.3—51. eq.

Arrhenius' equation is the result of curve fitting to experimentally available points as illustrated in Figure 1.1.3—8:

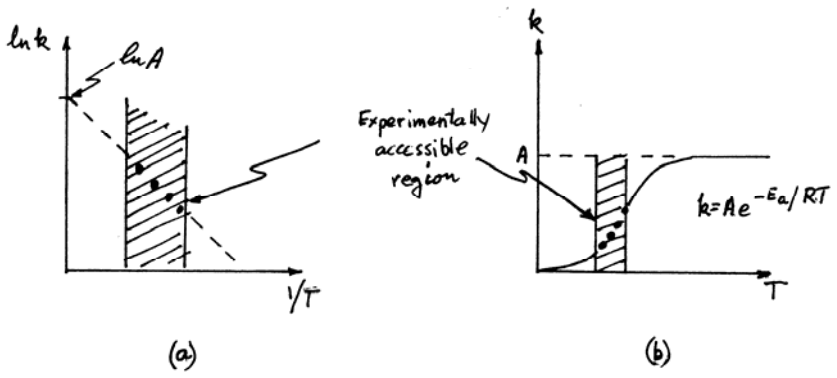


Figure 1.1.3—8. Logarithmic (a) and nonlogarithmic (b) plots of the rate constant against reciprocal absolute temperature (a) and absolute temperature (b), respectively.

In the Arrhenius's equation, the pre-exponential factor is assumed to be independent of T. In contrast, the transition state theory stipulates that the pre-exponential factor depends on T:

$$k = \frac{RT}{Nh} e^{-\Delta G^{\ddagger}/RT} = \frac{RT}{Nh} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$$

1.1.3—52. eq.

Dividing both sides of 1.1.3—52. eq. by T and taking the log to base 10 of both sides we obtain 1.1.3—53. eq.:

$$\log\left(\frac{k}{T}\right) = -\left(\frac{\Delta H^{\ddagger}}{2.303R}\right)\frac{1}{T} + \log\left(\frac{R}{Nh}\right) + \frac{\Delta S^{\ddagger}}{2.303R}$$

1.1.3—53. eq.

$$\log\left(\frac{k}{T}\right) = -\left(\frac{\Delta H^{\ddagger}}{4.573}\right)\frac{1}{T} + 10.319 + \frac{\Delta S^{\ddagger}}{4.573}$$

1.1.3—54. eq

If natural log (i.e. ln) is used instead of log of base 10 then the conversion factor (2.303) will not appear in equation 1.1.3—53. eq.

An example of the determination of the energy of activation (Ea) according to 1.1.3—51. eq., and the enthalpy of activation ($\Delta H^{\ddagger}$) as well as the entropy of activation ($\Delta S^{\ddagger}$) according to 1.1.3—54. eq, is shown for a typical case in Figure 1.1.3—9.

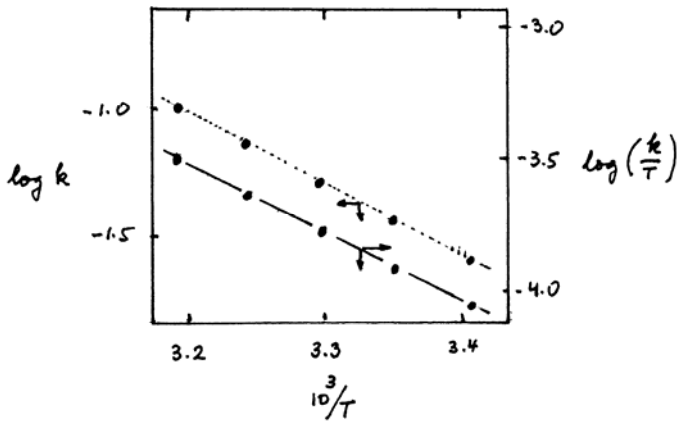


Figure 1.1.3—9. Determination of energy of activation (E_a ·····), and enthalpy of activation ($\Delta H^{\ddagger}$ ----) for the reaction MeSPh +$NaIO_4$ → MeS(O)Ph + $NaIO_3$

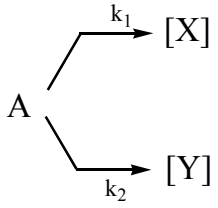
The Arrhenius-type energy of activation (E_a) and enthalpy of activation ($\Delta H\ddagger$) are related to each other according to equation 1.1.3—55. eq.

$$E_a = \Delta H^{\ddagger} + RT$$

1.1.3—55. eq.

Since RT at room temperature is about of 0.6 kcal mol^{-1} or 2.51 kJ mol^{-1}, the numerical values of E_a and $\Delta H^{\neq}$ are usually close to each other.

As discussed earlier, for parallel (i.e. competing) reaction mechanisms the product ratio at any time during the reaction is also the rate constant ratio. This may be used to calculate the differences in the activation parameters, $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$, as shown in 1.1.3—58. eq.:



1.1.3—56. eq

$$\frac{[X]}{[Y]} = \frac{k_1}{k_2} = \frac{\frac{RT}{Nh} e^{\Delta S_1^{\ddagger}/R} e^{\Delta H_1^{\ddagger}/RT}}{\frac{RT}{Nh} e^{\Delta H_2^{\ddagger}/R} e^{\Delta H_2^{\ddagger}/RT}}$$

1.1.3—57. eq

$$\log\frac{[X]}{[Y]} = -\left(\frac{\Delta H_1^{\ddagger} - \Delta H_2^{\ddagger}}{2.303R}\right)\frac{1}{T}\left(\frac{\Delta S_1^{\ddagger} - \Delta S_2^{\ddagger}}{2.303R}\right)$$

1.1.3—58. eq.

In closing this section, we might add that for a reaction, in which the Transition State is more disordered than the Reactant State, the entropy change is expected to be positive. This is the case for S_N1 and E1 reactions. In contrast to this if the disorder is reduced when the system reaches the Transition State, then the entropy change is expected to be negative. This is the case for S_N2 and E2 mechanisms.

$$\Delta S > 0 \text{ (for } S_N1 \text{ and E1)}$$

1.1.3—59. eq

$$\Delta S < 0 \text{(for } S_N2 \text{ and E2)}$$

1.1.3—60. eq

This expectation is illustrated in Table 1.1.3-4 for the following hydrolytic reactions following either the S_N1 or S_N2 mechanisms

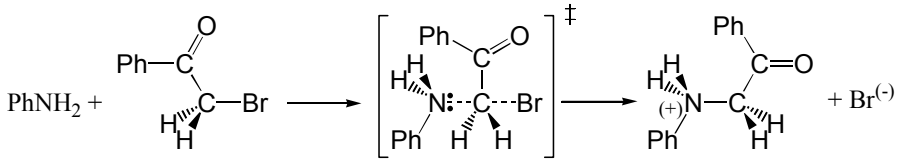
$$R{-}L + H_2O \rightarrow R{-}OH + LH$$

1.1.3—61. eq

Table 1.1.3-4. Activation parameters for unimolecular (S_N1) and bimolecular (S_N2) hydrolysis of alkyl halide-type compounds.

Compounds	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol deg)	Mechanism
Me-Cl	25.3	-8.6	S_N2
Me-Br	24.1	-6.7	S_N2
iPr-Cl	24.9	-5.3	S_N2
iPr-Br	24.4	-1.4	S_N2
tBu-Cl	20.5	+3.4	S_N1
tBu-$SMe_2^{(+)}$	31.6	+15.7	S_N1

The numerical value of $\Delta S^{\ddagger}$ is also dependent on solvent polarity. The value of $\Delta S^{\ddagger}$ in a polar solvent is usually a smaller negative number than in an apolar solvent. In the case of an apolar solvent, the formation of the solvation shell represents an appreciable increase in order, whereas a polar solvent is already well ordered and no marked change will take place due to solvation. For this reason, to reach the Transition State in apolar solvents the entropy must decrease more than it does in polar solvents. This phenomenon is illustrated for the following S_N2 reaction mechanism 1.1.3—62. eq. in table 1.1.3-5[9].



1.1.3—62. eq.

Table 1.1.3-5. Activation parameters determined in various solvents for the reaction $PhNH_2$ + Br - CH_2CO-Ph →[Ph - NH_2 - CH_2-CO - Ph]$^{(+)}$ $Br^{(-)}$

Solvent	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$ cal/mol deg.
C_6H_6	7.5	-56
$HCCl_3$	10.2	-46
Me_2CO	10.5	-39
MeOH	11.8	-33
EtOH	13.3	-28

Appendix

To solve exercises we used Gaussian03 ab-initio program package. Other ab-initio programs and free demos can be found in the next location

http://www.theochem.uni-stuttgart.de/theolinks/links.html below the Program Packages and Documentations Ab initio program packages titles

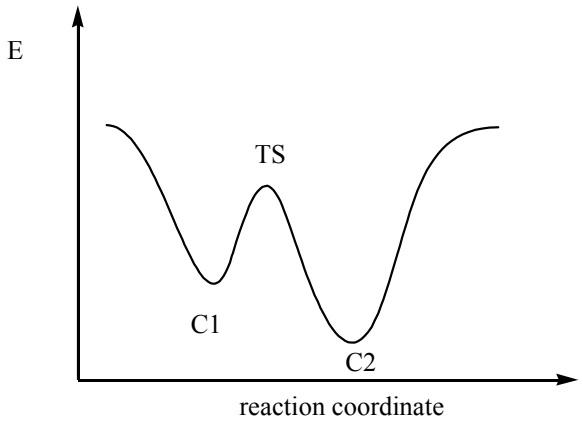
Appendix 1

Problem

Compute the energy profile of the concreted (A) and stepwise (B) mechanism of reaction between metil-cloride and Brom ion.

Solution of S_N2 (concreted) reaction.

To solve this problem we use Gaussian 03 and gview programs.
As we calculate the energy in gas phase the energy profile is similar to the next



First we have to optimize the starting complex (C1) and product complex (C2). One of the input files is below

```
%chk=SNopt.chk
%mem=6MW
%nproc=1
```

```
#p opt hf/3-21g                                          optimization at 3-21g basis set

Metilklorid - bromide ion kiindulasi complex(C1) optimizacioja     note

-1 1                                                     charge -1, multiplicity singlet
C          0.61552264   0.78757807   0.54621719        atomic coordinates in Cartesian frame
H          0.97217707  -0.22123193   0.54621719
H          0.97219548   1.29197626   1.41986870
H          0.97219548   1.29197626  -0.32743431
Cl        -1.14447736   0.78759976   0.54621719
Br         3.84149447   0.83548548   0.70019980
```

Then we make a redundant coordinate between the Brom ion and carbon atom of metil-cloride. During the optimization we increase the distance between the two atoms with 0.01Å in each step.

```
%chk=
%mem=6MW
%nproc=1
#p opt=modredundant hf/3-21g geom=connectivity     optimization at 3-21g basis set

SN reakció scan a szén-bromion tavolsag csökkentésével

-1 1

C                                                 atomic coordinates in Z-matrix form
H          1        B1
H          1        B2   2        A1
H          1        B3   2        A2   3        D1
Cl         1        B4   4        A3   3        D2
Br         1        B5   4        A4   3        D3

 B1        1.06717105
 B2        1.06718052
 B3        1.06716759
 B4        1.99526909
 B5        3.11779504
 A1      114.18106258
 A2      114.19157479
 A3      104.19767784
 A4       75.81809217
 D1      133.94956808
 D2      113.03179128
 D3      -66.94632404

1 2 1.0 3 1.0 4 1.0
2
3
4
5
6
                                                  redundant parameters: Bond between atom no.6 and 1
step no.150
B 6 1 S 150 -0.010000                             step -0.010000Å
```

You can see the results in the gwiev. You have to choose in the open dialog box read intermediate geometries and open the out file. If in the results dialog box you choose the scan option you will get a diagram of C-Br distance versus Energy of molecule. The diagram is false after the second minima, because the C-Br distance too short, so we have to calculate with other redundant coordinate.

Appendix 2

Problem: Use Gaussian X program package to compute the dipole momentum of following species: CH_4, C_2H_6, C_3H_8, Butan (4 conformers), MeCl, MeBr, MeF, MeOH, MeSH, $MeNH_2$, MeMgCl.

Solution: Input file for methane:

```
%chk=metan.chk
%mem=6MW
%nproc=1
#p opt hf/3-21g

Methan dipole moment

0 1
 C
 H                  1             B1
 H                  1             B2    2              A1
 H                  1             B3    3              A2    2
D1
 H                  1             B4    3              A3    2
D2

   B1             1.07000000
   B2             1.07000000
   B3             1.07000000
   B4             1.07000000
   A1           109.47120255
   A2           109.47125080
   A3           109.47121829
   D1          -119.99998525
   D2           120.00000060
```

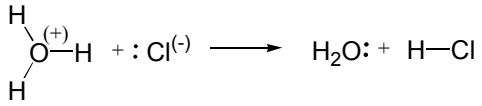
Results:

Species	Computed
Metane	0 debey
Ethane	0 debey
Propane	0 debey

Butane	
Syn-periplanar	0.0570 debey
Syn kinalis	0.0446 debey
Anti kinalis	0.0627 debey
Anti-periplanar	0.0 debey
Metilcloride	2.8641 debey
Metilbromide	2.1624 debey
Metilfluoride	2.3393 debey
Metilhidroxide	2.1227 debey
Metilsulfit	2.1178 debey
Metilamin	1.4401 debey
Metilmagnezium klorid	3.5176 debey

Apppendix 3

Problem: Compute the energy of species involving in the following reaction:



Solution:
Input file for H_3O^+

```
%chk=h3o.chk
%mem=6MW
%nproc=1
#p opt=gdiis hf/3-21g

Oxonium ion molecule energy cal.

1 1
 O
 H                  1             B1
 H                  1             B2    2             A1
 H                  1             B3    2             A2    3
D1

   B1             0.96000000
```

```
   B2              0.96000000
   B3              0.96000000
   A1            109.47122063
   A2            109.47122063
   D1            120.00000000
```

Species	Energy in a.u.
H_3O^+	-75.89122771
Cl^-	-457.35358538
H_2O	-75.58580978
HCl	-457.86943112

Appendix 4

Problem: Calculte the energy curve of reaction path HCl-water cluster dissociation.
Solution: let change the O-H distance between the oxygen of water and hydrogen of HCl with 0.05Å increments. (Use add rendundant coordinates)

Input(.gjf) file for G03 program

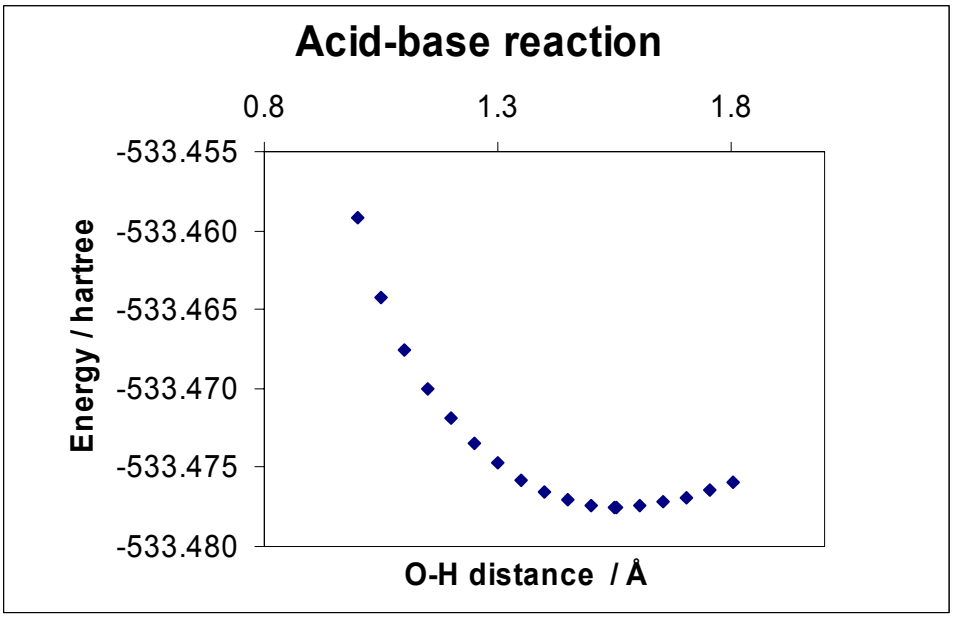
```
%mem=350MB
#p opt=modredundant rhf/3-21g

viz+HCl scan                                          #notes

0 1                                                #charge 0, multiplicity
singlet

 O                  1.78455000   -0.00002200   -0.03620000 #geometry in
 H                  0.23080100   -0.00039200   -0.03276400 #Cartesian
 H                  2.30247100    0.79701900    0.12932800 #frame
 Cl                -1.12428900    0.00000500    0.00374200
 H                  2.30323800   -0.79653800    0.12943000

B 2 1 S 20 0.050000 0.800000 1.800000     #scan the bond between the atom 1
and 2
                                          #in 20 steps with 0,05 increments
                                          #between 0,8 and 1,8 Å
```


Acid-base reaction
0.8
1.3
1.8
-533.455
-533.460
-533.465
-533.470
-533.475
-533.480
Energy / hartree
O-H distance / Å

Literature

[1] Ruff, Csizmadia Fizikai szerves kémia
[2] IGC tol meg kell kerdezni
[3] Ionradius data and energetic of NaCl solvatation.
[4] Elektronegativitas scaling factor
[5]Kotesi energiak azempirical modszerekben
[6] pKa ertekek szenhidrogenekre
[7] Szupersavak H0 ertekeik
[8] Ethan pka erteke
[9] PhNH2 es br fenilacetat rekcioja kulonbozo oldoszerekben.

Proposed literature

Bruchner Szerves kémia
Solomons Organic chemistry
Veszprémi Kvantumkémia