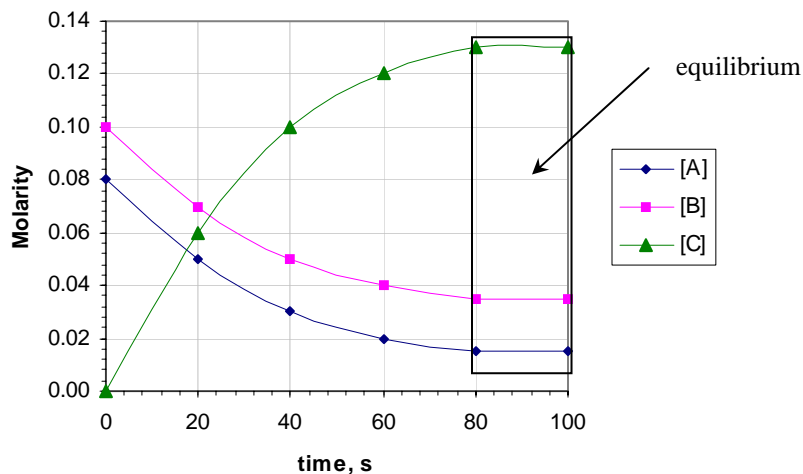


Determining the Equilibrium Constant for an Esterification

Background

Although we tend to speak of chemical processes as if they always went to "completion" we know that many reactions give incomplete yields for a variety of reasons. In some cases there are competing processes which use up reactants but in most cases where completion is not achieved the reaction settles into an *equilibrium* condition. The concentrations of reactants gradually decrease while the concentrations of products increase until all become constant (but not zero).

Concentration Changes for $A + B \rightleftharpoons C$



Visually equilibrium may look like completion unless there are cues in the reaction system (e.g., color) which indicate that reactants remain when there are no further changes observed. Even if we are tempted to conclude that the reaction simply stopped "short", in many cases it is a fairly simple matter to demonstrate that the reaction system remains dynamic, i.e., the reaction continues to occur in *both* directions. Changes in conditions of temperature, pressure and concentration can in fact "move" the equilibrium "position" forward or backward (LeChâtelier's Principle).

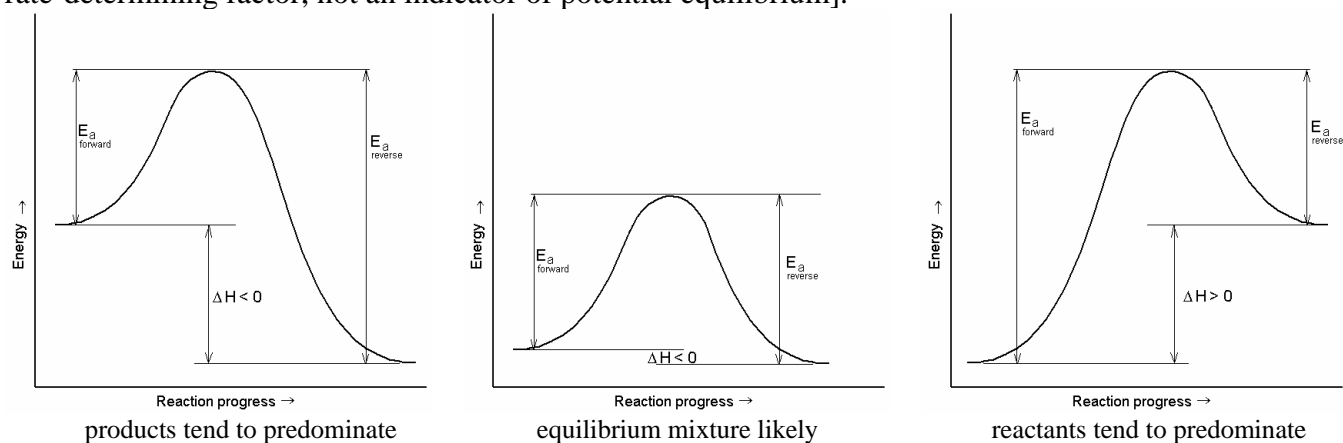
Experimental observations therefore reveal the criteria for maintaining a system in equilibrium (assuming the system has the potential to reach equilibrium as opposed to going to completion): constant temperature and a closed system. But why is there equilibrium in the first place? Why don't all chemical processes continue until at least one of the reactants has been exhausted?

Theoretically all reactions are reversible, i.e., under some conditions it should be possible to make either the forward or reverse reaction occur. Practically speaking this is not true for some processes and is "less true" for others. In searching for characteristics of potential equilibrium systems it is helpful to consider the kinds of reactions which go essentially to "completion", i.e., chemical systems in which the reverse reaction is negligible for practical purposes at standard conditions.

The formation of an additional phase during a reaction is a classic indication that the forward reaction will *usually* proceed so far to the right as to be considered "complete". Examples include precipitations and gas formations. Even among these types there are common exceptions but they do point to at least one aspect of what is happening at equilibrium: *in order to have a reverse reaction of any significance the products should ideally remain in the same phase system*. This is a consequence of simple collision theory. Molecules can't collide and react with something that is gone.

This insight suggests that homogeneous systems are better candidates for practical equilibrium. Many gaseous systems fit this description, from the equilibrium between NO_2 and N_2O_4 to the synthesis of ammonia from elements. As long as all of the molecules are able to move freely in the reaction mixture one collision possibility is as good as another. Or is it?

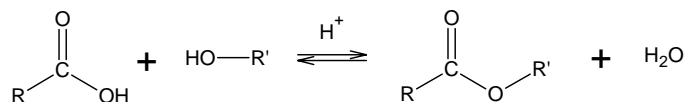
We know that according to collision theory not all collisions are created equal. Some molecular collisions require large amounts of energy in order to be effective (i.e., result in reaction). We say the reactions involving these collisions have high *activation energies*. Ignoring other possibly significant factors temporarily, it should then make some sense that reactions with "smaller" enthalpy changes are more likely to reach practical equilibrium rather than practical completion. When the enthalpy change for a reaction is "small" the activation energies of the forward and reverse processes are more nearly equal. So it seems likely that all of the collisions have roughly "equal" footing [note that it doesn't matter that the activation energies are either large or small, only that they are *similar*; the magnitude of E_a is a rate-determining factor, not an indicator of potential equilibrium].



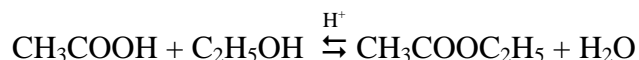
Of course, this is a great oversimplification. In addition to the energy requirements for an effective collision there are geometry factors that are not easily predictable. This variable brings analyses starting from the enthalpy-only perspective into the realm of "I can see why this reaction reaches equilibrium" after you know already that it does!

An important factor not mentioned is, of course, entropy. As a reaction proceeds, the free energy in the system gradually decreases. When no more free energy can be moved from the system to the surroundings no further net chemical change occurs. At what mixture of reactants and products this occurs is partially dependent on the entropy change during the reaction. It is not difficult to imagine that homogeneous systems with a *mixture* of reactants and products have a generally greater entropy than systems containing only products. But the interplay between the magnitude (and sign) of the enthalpy change in the system and hence the entropy change in the surroundings makes this kind of analysis complex and not easily generalized. That is, after all, what standard free energy changes are good for: deciding whether reactions will be very spontaneous (i.e., go to "completion") or only so-so spontaneous (i.e., reach practical equilibrium). An appreciation of some of the factors which go into favoring equilibrium over "completion" is valuable nonetheless for the insight it offers into the complex nature of the interaction of matter with energy at the molecular level.

Determining the value of an equilibrium constant for a reaction in the laboratory can present some interesting challenges. Measurements on the system must either be non-intrusive (i.e., they must not result in changes which will cause a shift in equilibrium) or the reaction rate must be slow enough so that any equilibrium shift is negligible during the measurement. Many *esterifications* are slow at room temperature, even with catalysts. Recall that esterification is the reaction of a carboxylic acid with an alcohol:



The specific esterification reaction studied in this experiment is that between ethanoic acid (acetic acid) and ethanol:



The formation of ethyl ethanoate (ethyl acetate) is particularly well-suited to the determination of the equilibrium constant. The reaction is slow enough at room temperature so that the order of mixing, temperature fluctuations over two days of reaction time, and even a final titration with a strong base have little effect on the reaction. Since this is a homogeneous reaction with the same number of moles of reactants and products, the equilibrium constant, K_c --generally expressed in terms of Molarity--can be calculated in terms of moles alone--an added convenience.

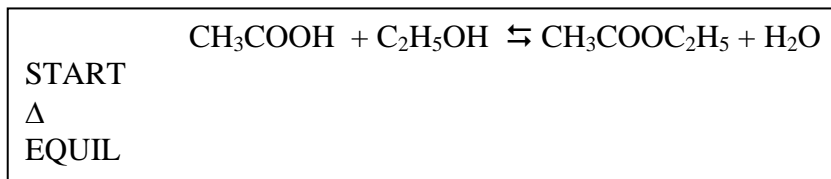
Because the reaction is very slow at room temperature, dilute HCl is added as a catalyst to speed it up. The HCl does not take part in the overall reaction, but the water found in the dilute acid *does* take part in the reaction and the number of moles of it added to a mixture must be taken into consideration.

To demonstrate that the equilibrium constant has in fact the same value, regardless of the starting amounts, a variety of mixtures can be prepared, each of which is then analyzed to determine the distribution of reactants and products in the equilibrium mixture. We know from LeChâtelier's Principle that adding more of one reactant at the beginning of an equilibrium process should result in a greater yield of product. It may not be as convincing that the overall ratio of the equilibrium constant will be the same as if the extra reactant has not been added. So the virtue of repetition in the lab can serve more than one purpose.

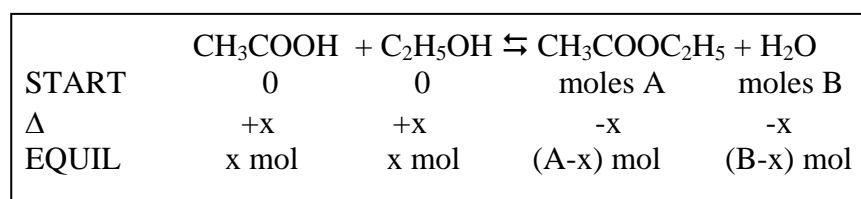
The analysis of the equilibrium mixtures is based on a simple titration with standardized NaOH. Since the initial amounts of all materials are known the final amount of acid determined will reflect the overall changes in the reaction. For example, the HCl catalyst remains unchanged. Once this amount of acid is subtracted out there remains only the ethanoic acid. If less acid is detected than was originally added then the reaction has moved in the forward direction. If more acid is detected then the reaction has moved in the reverse direction. Since the stoichiometric ratios in the reaction are all unity the loss or gain in ethanoic acid can be used to figure the loss or gain in everything else.

The calculations involved in determining the equilibrium constant in this experiment become quite complex due to the use of aqueous solutions of ethanoic acid and hydrochloric acid in a system in which water is a participant [a spreadsheet would probably be very useful for the repetitive calculations, but a long-hand series is not out of the question].

The simplest way to approach the problem is the familiar **start/equilibrium** set-up:



The starting moles of each substance may be determined from the table of suggested mixtures in the Technique section. Since the ethanoic acid is only 99% (by volume) this must be taken into account for accurate work (the remaining 1% is water). The ethanol used is also only 95% (by volume) [the remainder is other non-aqueous material which may be ignored]. The amount of water added with the HCl catalyst must also be added to the initial water moles. In the first mixture which is composed only of ethyl ethanoate and the HCl catalyst (mainly water), the reaction is expected to proceed to the left. This would result in the following set-up:



But how much is **x**? The titration of the equilibrium mixture will reveal how much acid is present. Part of that acid is the HCl catalyst added to each mixture (this is the "blank"). The volume of NaOH required to titrate just this acid will be known from the data and can be subtracted from the total volume of NaOH used to titrate each mixture. The remaining NaOH required is a measure of the amount of ethanoic acid present, in this case, **x**.

The Experiment

There are three parts to this experiment:

- preparation of the various mixtures
- standardization of the sodium hydroxide
- titration of the equilibrium mixtures

The following non-locker materials will be provided:

- ethyl acetate (ethyl ethanoate)
- glacial acetic acid (ethanoic acid) [fume hood]
- concentrated HCl [fume hood]
- micropipettor w/tips
- 8 vials
- approx. 1 M NaOH
- solid potassium hydrogen phthalate
- phenolphthalein
- beral pipets

The Chemicals

Ethanol or ethyl alcohol is a clear, colorless liquid with a pleasant odor and a burning taste. It absorbs water readily from the air and is miscible with water and many organic liquids. Most ethanol is used in alcoholic beverages in dilute form. It is also used in the laboratory as a common solvent, in pharmaceuticals, and as a common topical antiseptic. Nearly all ethanol sold as "alcohol" (not for drinking) has been *denatured* (including the ethanol in the lab). Denaturing in this context means adding some substance which does not markedly interfere with the behavior or properties of ethanol except to render it unfit for drinking. Most denaturants are toxic.

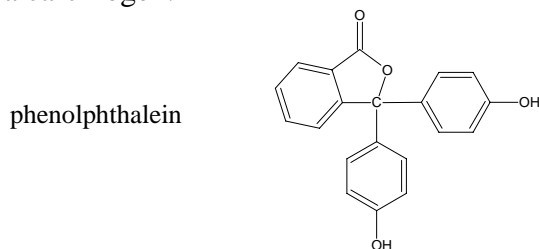
Acetic acid (or ethanoic acid) has a pungent odor and in concentrated form (17 M) produces painful burns on the skin. It is soluble in water and is itself an excellent solvent for many organic compounds. While it is a weak acid, concentrated solutions are extremely irritating to tissue, especially mucous membranes. It is used in the manufacture of various acetates including plastics and textiles, in dyeing, preserving foods and in many organic syntheses. Household vinegar is 5% acetic acid. Ingestion of more concentrated solutions may cause severe corrosion of the mouth with vomiting, circulatory collapse and eventual death.

Ethyl acetate has a characteristic fruity odor and a pleasant taste when diluted. It is somewhat soluble (1 mL in 10 mL) in water and mostly soluble in common organic solvents. It is used in artificial fruit essences and as a solvent for lacquers and varnishes (including fingernail polish). Prolonged breathing of vapors may cause liver and kidney damage.

Sodium hydroxide is commonly known as lye or caustic soda. It is a very hygroscopic white solid (absorbs water from the air rapidly) and also absorbs CO₂. It is very corrosive to vegetable and animal matter and aluminum metal, especially in the presence of moisture. Dissolving NaOH in water generates considerable heat.

Besides its use in the laboratory, sodium hydroxide is used in commercial drain cleaner preparations, to treat cellulose in the manufacture of rayon and cellophane and in the manufacture of some soaps. It is corrosive to all tissues and can be detected on skin by the "slimy" feeling associated with bases. It should be rinsed off thoroughly upon contact. It can damage delicate eye tissues and cause blindness.

Phenolphthalein (or 3,3-bis(*p*-hydroxyphenyl)phthalide), C₂₀H₁₄O₄, is a white powder or minute crystals and almost insoluble in water. One gram dissolves in 12 mL of alcohol. A 1% alcoholic solution is commonly used as an indicator in titrations of mineral and organic acids with most bases. It is not suitable for ammonia. It is very sensitive to CO₂, decolorizing slowly from its basic pink form on exposure to air. Colorless to pH 8.5; pink to deep red above pH 9. It has been used in the past as a laxative (the former active ingredient in Ex-lax and many other similar preparations) but recent studies have implicated it as a carcinogen.



Potassium hydrogen phthalate (or potassium biphthalate), $\text{KOOCC}_6\text{H}_4\text{COOH}$, consists of white crystals, stable in air. It is soluble in about 12 parts of cold water, only slightly soluble in alcohol. The salt is used as a primary standard for preparing volumetric base solutions and also in buffer solutions.

Technique Discussion

The experiment may be conveniently divided into three parts which must be done in sequence due to the time required for the equilibrium reaction. First the various mixtures must be prepared [table follows]. One of the ingredients, the dilute HCl, must be made before the mixtures can be assembled. Once the solutions are made they are capped securely and set aside for 48 hours to equilibrate.

During the equilibration process the NaOH solution (which is supplied in only approximate concentration) can be standardized by titration against dried KHP. These titrations should be done in triplicate (standard practice). Because of the scale of the experiment the use of a buret is impractical. Drop titration from a beral pipet is adequate for the accuracy expected from the determination. The density of the NaOH will be supplied so the initial and final mass of NaOH [rough balance] can be used rather than a count of drops.

Finally, after the 48 hours have elapsed the mixtures (and blank) are titrated with the standardized NaOH employing the same mass-difference technique.

5 mL of approximately 3 M HCl acid solution is prepared by diluting a suitable volume of 12 M HCl with distilled water. *Remember, always add concentrated acid to water, not the reverse!* Do this in the fume hood. To facilitate the calculation of the amount of water added with the HCl catalyst the density of the mass of 0.500 mL will be useful [analytical balance].

The following table contains the proportions for the mixtures.

Mixture	3 M HCl	Ethyl Acetate	Ethanol	Acetic Acid	Water
A	0.500 mL	0.500 mL	-	-	-
B	0.500 mL	0.400 mL	-	-	0.100 mL
C	0.500 mL	0.200 mL	-	-	0.300 mL
D	0.500 mL	0.400 mL	0.100 mL	-	-
E	0.500 mL	0.400 mL	-	0.100 mL	-
F	0.500 mL	-	0.400 mL	0.100 mL	-
G*	0.500 mL	-	-	-	0.500 mL

*blank

A little more than 0.20 g [rough balance] of solid potassium hydrogen phthalate (KHP) in about 20 mL of water can be used to standardize the approximately 1 M NaOH solution. This should be done three times. KHP is a little slow to dissolve in water so if there is time left on the day the mixtures are prepared these samples could also be made and left to dissolve overnight.

[ordinarily this process would be done on the analytical balance but the results of this experiment do not justify the precision gained]

When 48 hours have elapsed, solutions A through G should be titrated with the standardized NaOH. **Be extremely careful not to pass the endpoint which will be different in each case. You only get one chance!** Remember the solution should be the palest persistent pink possibly perceptible which may fade on standing for longer than 1 minute.

The Report

Your initial calculations should include:

1. The concentration of the standard NaOH, shown in triplicate determinations
[best value/standard deviation, 95% confidence]
2. Using densities, the initial moles of each substance involved in the reaction for each mixture
[a table would be helpful]
3. From the titration data, the moles of acid neutralized in each mixture (with the blank subtracted)
4. The START/EQUIL set-up for each reaction mixture [see Background for example]
5. The equilibrium constant for each mixture
6. The average equilibrium constant
[apply the Q -test and then determine the best value/standard deviation, 95% confidence, with the values you do not reject]

Your conclusion to this experiment should include a brief explanation for any significant deviations of duplicate results.