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EQUILIBRIUM STUDY OF THE
THREE COMPONENT SYSTEM
OXALIC ACID--SODIUM OXALATE--WATER AT 25°

BY
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INTRODUCTION

The experimental measurement of chemical equilibria frequently presents problems of considerable difficulty. In some cases the position of equilibrium may be such that the reaction goes nearly to completion in one direction, resulting in an extremely small concentration of one or more of the reactants. In other cases the rate of the reaction may be so slow that equilibrium is not established in any convenient time at some desired temperature. Then again, the rate of the reaction may be so rapid that an attempt to analyze the equilibrium mixture will result in a shift in equilibrium. Especially in the reactions of organic chemistry, as also in many inorganic reactions, the problem is complicated by the presence of side reactions other than those of which the equilibrium we wish to measure. Finally, the presence of new compounds, the determination of their complexity, and the conditions necessary for their formation makes the study one of great interest and value.

Study of equilibria has contributed toward a more systematized classification of the science of

chemistry. At the same time it has helped to establish chemistry as an indispensable foundation of modern industrial achievement.

HOMOGENEOUS EQUILIBRIA AND THE

LAW OF MASS ACTION

The great majority of chemical reactions are of such type that they do not go entirely to completion. Instead, at some point, a reverse action occurs which proceeds at the same rate as the forward reaction. Such a state is referred to as the state of "dynamic equilibrium". The esterification of acetic acid with ethyl alcohol serves as an illustration that exhibits this phenomenon. If equimolecular amounts of the two reactants are mixed at laboratory temperature, two-thirds of the mixture is converted to ethyl acetate and water. One-third remains unchanged no matter how long the substances are left in contact. In the written equation this tendency is notated by a double arrow which replaces the usual one-way symbol; and the degree of this tendency by the length; thus



The conditions of equilibrium at a given temperature, in such cases of simple equilibrium, can be obtained by applying the law of mass action which was first clearly stated by two Norwegian scientists, Guldberg and Waage.⁶ On applying this law to reactions taking place in a homogeneous system at constant conditions, it has been found that the velocity with which two compounds react

is statistically proportional to their concentrations. With the general equation



we can use the expression $v_1 = k_1 [A]^a [B]^b$ where k_1 is a velocity proportionality constant and the brackets indicate molecular concentrations. Similarly, the velocity of the reverse reaction is expressed by $v_2 = k_2 [C]^c [D]^d$. When the state of dynamic equilibrium is reached, the velocities of both reactions are equal. Therefore, $v_1 = v_2$ or $k_1 [A]^a [B]^b = k_2 [C]^c [D]^d$ and the following expression of K , the equilibrium constant, results.

$$K = \frac{k_1}{k_2} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (3)$$

Such an equation, then, gives the conditions of equilibrium at constant conditions. The superscripts indicate that each concentration is raised to power equal to the number of moles of each substance taking part in the reaction.

Although this derivation represents the constant as a ratio of velocity coefficients, it can also be calculated from thermodynamics and chemical kinetics. G. N. Lewis¹⁰ substituted activities for concentration. The activity is a number which is related to the concentration of a substance and is expressed as the **product** of the concentration and an activity coefficient which is itself

dependent on concentration.

The effect of temperature and pressure on any of these systems can be predicted qualitatively by the use of the Le Chatelier theorem or by van't Hoff's law of mobile equilibrium.

Quantitative effect of temperature can be calculated from heats of reaction by means of the expression known as the van't Hoff isochore.¹⁰ The equation takes the form

$$\frac{d \ln K}{d T} = \frac{\Delta H}{RT^2} \quad (4)$$

where H equals the heat of reaction. If this heat value is assumed to be a constant over a desired range, the integration of the equation yields

$$\log \frac{K_1}{K_2} = \frac{\Delta H (T_2 - T_1)}{(2.303)(1.987)(T_1 T_2)} \quad (5)$$

Therefore if the heat of reaction is known, one can calculate K_2 when K_1 is known. Conversely, if the values of both K_1 and K_2 are known, one can calculate the heat of reaction.

HETEROGENEOUS EQUILIBRIUM

AND THE PHASE RULE

Even in cases of some heterogeneous systems, i.e., systems made up of physically distinct parts, the law of mass action can be applied, provided that it can be assumed that the heterogeneous equilibrium is dependent on equilibrium in a single phase.

The law, however, cannot be applied to many heterogeneous systems in which we know neither the resulting compounds nor their complexity. For these we use the general theorem, enunciated by J. W. Gibbs, which we know as the Phase Rule.⁴ This rule defines the conditions of equilibrium in an heterogeneous system as a relation between the number of phases and the components of that system. It can be stated: The number of degrees of freedom possessed by a system in equilibrium is equal to two more than the number of components minus the number of phases.³ Mathmatically it takes the form

$$F = (C + 2) - P \quad (6)$$

where F is the number of degrees of freedom, C is the number of components, and P is the number of phases. The term 2 is generally included because in most cases a system has only two other variables (temperature and pressure) in addition to composition. If, for instance,

the pressure has no influence on the equilibrium, then the only other variable besides composition is the temperature, and the numeral becomes 1. Inversely, if other forces, such as electrical or gravitational, affect the equilibrium, the numeral increases.

The number of components of a system is defined as the smallest number of chemical substances which is necessary fully to define the **system** chemically. The phases are those homogeneous parts of a system which are separated by definite, physical boundaries. By substitution in the phase rule we determine the number of conditions which can be altered without causing the appearance or disappearance of a phase. Thus, dealing with three components existing in two phases (as is the case in this presentation) the equation yields,

$$F = 3 + 0 - 2 = 1$$

Such a system would have one degree of freedom. The state of the system would be undefined unless three of the variables were fixed.

It is important to remember that the phase rule applies only to systems which are in equilibrium. The presence of equilibrium is ascertained if the same conditions are reached from whichever side it is approached. The rule is one of great importance for it not only gives

the conditions under which heterogeneous equilibrium can exist but, due to the fact that it is derived purely from a thermodynamic basis, it is independent of any changing theories or hypotheses. The rule further enables us to establish a classification of chemical systems according to their degrees of variance.

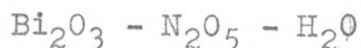
THREE-COMPONENT SYSTEMS

In passing to systems of three components, it is well to keep in mind all relations between components, variables, and degrees of freedom outlined in the previous section. No new principles are involved excepting possibly to note the general types of reacting systems which are classified under the heading of three-component.

Perhaps the most commonly studied cases are those consisting of water with two salts having a common ion (sodium chloride--potassium chloride--water). Such systems if they react at all to form new compounds, can have them only of a composition between that of the three components. These new compounds then, can be classified as double salts or as hydrates which can be expressed in terms of the three components already present. It is interesting to note that a system consisting of water and two salts with no common ion, would at equilibrium no longer consist of three components. This becomes clear if we visualize a double decomposition occurring which will produce new compounds that cannot be expressed as combinations of the original components. These cases represent more complex systems.

Still another common type of ternary system consists of water and a single salt which undergoes hydrolysis

forming either acid or basic salts whose composition is not intermediate between the salt and the water. Such a system is a solution of bismuth nitrate which yields



In dealing with three-component systems completely, treatment should include equilibrium systems in which is present a vapor phase as well as solid and liquid phases. Here, however, we shall confine ourselves to condensed systems in which the gas phase is not present.

A complete representation of all variables in ternary systems (pressure, temperature, and two concentrations) would be a complex problem if at all possible. In most work which has been accomplished up to now such a complete representation is not necessary since the systems are studied under constant temperature and pressure. The problem then, is to represent the concentrations as the only variables. The most desirable device proposed is a geometric representation of composition on triangular coordinates. According to the method proposed by Gibbs⁴ an equilateral triangle is chosen. The composition of each pure component is represented by one of the vertices. A leg drawn from the vertex to the opposite side expresses 100% concentration of that component. A point along any side represents a binary compound whereas a point within the triangle represents a ternary compound.

With this method in mind we can now examine the system of bismuth nitrate to illustrate the method of graphing and to give some idea as to the complexity of ternary systems.

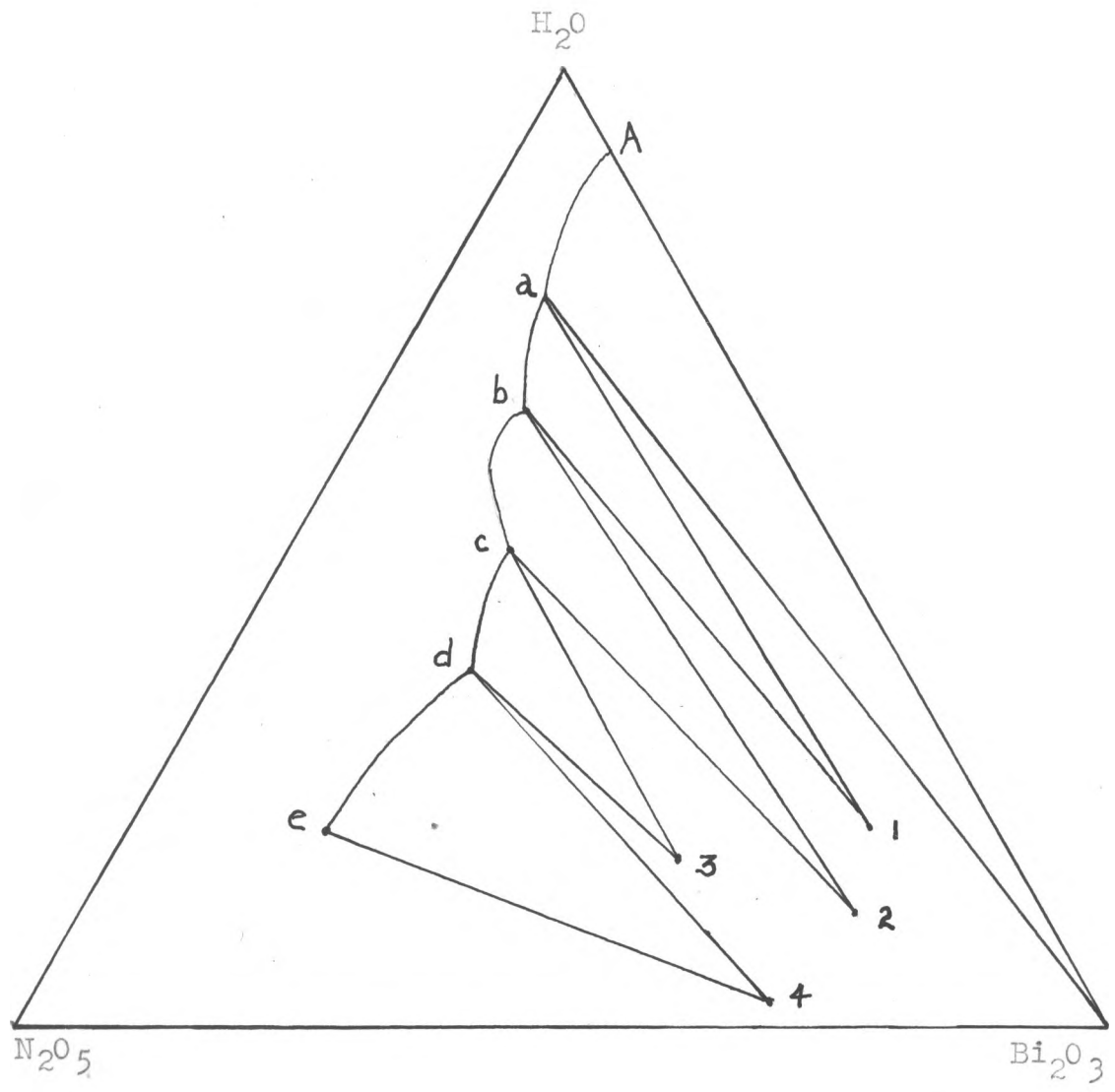
Taylor¹¹ gives the composition of the resulting compounds in a saturated solution as follows:

1. Basic salt hydrate - $\text{BiONO}_3 \cdot \text{H}_2\text{O}$
2. Basic salt hydrate - $\text{Bi}_2\text{O}(\text{NO}_3)_2 \cdot (\text{OH})_2$
3. Normal salt hydrate - $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$
4. Normal salt hydrate - $\text{Bi}(\text{NO}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$

Analysis of the solution yields composition points which when plotted on the triangular coordinates (Figure I) give the solubility curves, Aabcde, of the compounds in the presence of one another. The areas above the solubility curves indicate an unsaturated solution. Analysis of the residue yields points which when connected to corresponding points on the solubility curve, and extended, intersect at the points indicating the compositions of the resulting combinations. These points (1, 2, 3 and 4) represent ternary compounds of the following compositions:

1. $\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$
2. $\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$
3. $\text{Bi}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$
4. $\text{Bi}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$

THE SYSTEM $\text{Bi}_2\text{O}_3\text{-N}_2\text{O}_5\text{-H}_2\text{O}$



Ae - Solubility Curves
 • - Compositions of Hydrates

FIGURE I

THE SYSTEM

OXALIC ACID--SODIUM OXALATE--WATER

The system used in this work consists of oxalic acid, sodium oxalate and water. It is one which could provide interesting study since a comparison and analogy with the oxalic acid-potassium oxalate--water system of Foote and Andrew,¹² indicates the possible existence of several different combinations in the equilibrium system.

Depending on the concentrations of the components in the different solutions, five of the simplest combinations include the original acid hydrate, the original salt and possibly its hydrate, and three combinations of the two, giving an acid salt and two acid salt hydrates. The simple combinations include:

1. Acid hydrate . - $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
2. Normal salt - $\text{Na}_2\text{C}_2\text{O}_4$
3. Acid salt - $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$
4. Acid salt hydrate - $\text{Na}_2\text{C}_2\text{O}_4 (\text{H}_2\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$
5. Acid salt hydrate - $(\text{Na}_2\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

EXPERIMENTAL

Apparati. Glass stoppered bottles, weighing bottles, beakers, constant temperature bath, burettes, pipettes, analytical balance and weights.

Chemicals. Chemically pure grades of oxalic acid, sodium oxalate, redistilled water, concentrated sulfuric acid, .003N phenolphthalein indicator, and standard solutions of sodium hydroxide and potassium permanganate.

Procedure. Preliminary preparations consisted of calibration of the apparati used, i.e. determination of balance sensitivity, and calibration of weights and burettes. A solution of sodium hydroxide was standardized using oxalic acid as the standard; that of potassium permanganate was similarly treated using sodium oxalate as the standard.

A series of six solutions was prepared ranging from 370 mg to 10 mg of sodium oxalate in 10 g of redistilled water. To each, in a glass-stoppered bottle, was added an excess of oxalic acid and kept in the water bath at $25^{\circ} \pm .02^{\circ}$ for a period of sixty hours. The object of the different proportions was to approach equilibrium from both directions.

Analysis of Solution. After the sixty hour period, assuming that equilibrium had been established, approximately 5 ml

samples of clear, saturated solution were weighed, diluted to 60 ml and analyzed for hydronium ion and total oxalate ion by volumetric methods. Percent of water was determined by difference.

The data for these analyses is included in Table I. When plotted on the coordinates (Figure 2), it gives the solubility curve of the system.

Analysis of Residue. The solubility of a compound which is capable of existing in several forms depends upon the particular form in which it is found with the saturated solution. The question of the composition of the solid phase was, **therefore**, of considerable importance. Although its identification presents little difficulty in the majority of cases, it sometimes happens that it can be made by a more or less indirect method. The main reason for this is that adhering solution cannot usually be completely removed and the analysis, consequently, does not give direct information of the necessary accuracy. Such was the case of the residue in this system.

The method used is one which has been used considerably for identification of the solid phase. It is known as the wet residue method of Schreinemakers.⁹ It is based on the principle that if an analysis is made of both the saturated solution and a mixture of the solution and the solid phase, the points so obtained when plotted

lie on a line which connects the solubility curve to the point representing the composition of the solid. Similar analyses of other saturated solutions made up originally of varying proportions of the components, locate other such lines. Since all lines so determined, when extended pass through the same point, their intersection definitely locates the composition of the solid phase.

Following this procedure of analysis, samples of the residue were partially dried by means of filter paper. The partially wet residue was then weighed, dissolved in 60 ml of water and analyzed in the same manner as the solution. The data from the residue analyses is included in Table I.

Only experiments 1, 2, 3 and 4 exhibit the presence of a binary combination. The tie lines connecting these points to corresponding points on the solubility curve intersect at a point indicating a binary compound consisting of 62% salt and 38% acid. (Figure 2). This corresponds closely to the formula $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$.

TABLE ITHE SYSTEM OXALIC ACID--SODIUM OXALATE--WATER AT 25°Analysis of Solutions

	Percent $\text{H}_2\text{C}_2\text{O}_4$	Percent $\text{Na}_2\text{C}_2\text{O}_4$	Percent H_2O
1	1.86	1.33	96.81
2	2.69	1.28	96.03
3	4.97	1.21	92.82
4	8.23	1.32	90.45
5	10.54	1.37	88.09
6	10.66	.90	88.44

Analysis of Residues

	Percent $\text{H}_2\text{C}_2\text{O}_4$	Percent $\text{Na}_2\text{C}_2\text{O}_4$	Percent H_2O
1	24.21	38.58	37.21
2	25.56	40.52	33.92
3	28.90	49.55	21.55
4	27.13	44.91	27.96
5	64.20	5.74	30.06
6	66.47	5.65	27.78

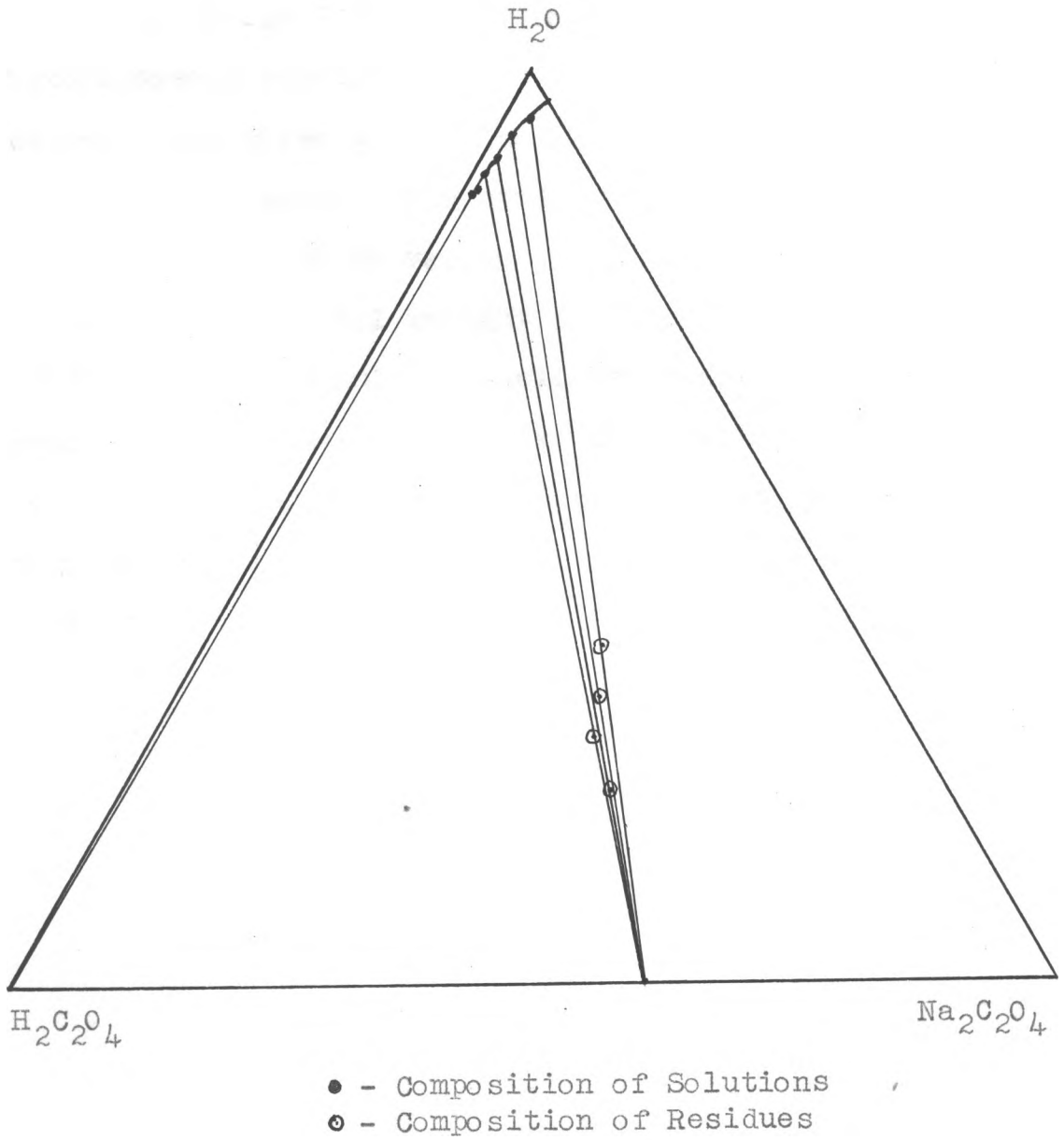
THE SYSTEM OXALIC ACID--SODIUM OXALATE--WATER AT 25°

FIGURE II

SUMMARY

A presentation has been made of the study of heterogeneous equilibria in ternary systems. Special emphasis was given the system of oxalic acid, sodium oxalate, and water. The study embraces a series of solutions, made up of varying concentrations of the three components, all brought to equilibrium at $25^{\circ} \pm .02^{\circ}$. The resulting equilibrium solutions were analyzed by volumetric methods; the residues by the residue method of Schreinamakers. The data indicates that under the conditions of this experiment a mixed salt of the composition $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ is formed.

Section 2
and 3

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