

Thesis Approved

By

C. L. Kenny Major Adviser

Thomas S. Bowdler Dean

✓  
A STUDY OF THE SOLUBILITY OF POTASSIUM CHLORIDE  
IN THE PRESENCE OF A STRONG ELECTROLYTE  
WITH NO COMMON IONS.

---

BY

JOSEPH E. KONON

---

A THESIS

Submitted to the Graduate Faculty of The Creighton University  
in Partial Fulfillment of the Requirements  
for the Degree of Master of Science  
in the Department of  
Chemistry

---

OMAHA, 1934

A Study of the Solubility of Potassium Chloride  
in the Presence of a Strong Electrolyte  
with No Common Ions.

1. Introduction

When a salt is in equilibrium with its saturated solution, the activity of the solid equals the activity of the salt in the saturated solution<sup>1</sup>.

At constant temperature and pressure, the activity of the solid will be a constant  $k'$ . Consequently under these conditions

$$k' = a_+^{v_+} a_-^{v_-} = \gamma_+^{v_+} \gamma_-^{v_-} (v_+ m_-)^{v_+} (v_- m_+)^{v_-} \quad (1)$$

where  $v$  = total number of ions

$v_+$  = number of cations

$v_-$  = number of anions

$a$  = activity

$\gamma$  = activity coefficient

$m$  = molality.

Since  $\gamma$  equals  $(\gamma_+^{v_+} \gamma_-^{v_-})^{1/v}$  we obtain

$$k = \gamma (v_+^{v_+} v_-^{v_-})^{1/v} (m_+^{v_+} m_-^{v_-})^{1/v} \quad (2)$$

which for heteronionic solvent becomes

$$k = \gamma (v_+^{v_+} v_-^{v_-})^{1/v} S \quad (3)$$

Now, let  $S_0$  and  $\gamma_0$  equal the solubility and activity coefficient in the saturated solution of the salt in the solvent not containing other salts, and  $S$  and  $\gamma$

equal the same quantities in the salt solutions. Then equation (3) becomes

$$S_0/S = \gamma/\gamma_0 \quad (4)$$

which gives the relation between molal solubility and activity coefficients.

For a homoionic solvent equation (2) becomes

$$k = \gamma(v_+^{v^+} v_-^{v^-})^{1/v} (S^{v^+} m_-^{v^-})^{1/v} \quad (5)$$

and, consequently,

$$v^+/v \log S_0/S + v^-/v \log m_0/m_- = \log \gamma/\gamma_0 \quad (6)$$

Recently Åkerlöf and Thomas making use of the above relationships, and others developed by them<sup>3</sup>, developed the equation

$$\begin{aligned} \log \delta_{\mu_T(S)} + k_1 + k_2(\mu_T - \mu_x) + v_1/v_1+v_2 \\ \log [v_3(\mu_T - \mu_x)^n + v_1\mu_x/n] = v_2/v_1+v_2 \log \mu_x/n = \\ \log \delta_{\mu_0(S)} + k_1\mu_0 + \log \mu_0 \end{aligned} \quad (7)$$

by which the solid phase of a mixture of two electrolytes may be determined. In the above equation  $\delta_{\mu_T(S)}$  = activity coefficient of a standard electrolyte in a pure water solution of the same ionic strength as the total ionic strength of the salt mixture.

$k_1$  = a constant relating the difference between the logarithm of the activity coefficient of an electrolyte in a pure water solution at the ionic strength  $\mu$ , and the activity coefficient of a standard electrolyte in a

pure water solution at the same ionic strength  $\mu$  to the ionic strength  $\mu$ .

$k_2$  = a constant relating the difference between the logarithm of the activity coefficient of an electrolyte in a mixture of electrolytes, the total ionic strength of the mixture being  $\mu_T$  and the activity coefficient of the same electrolyte in a pure water solution at an ionic strength  $\mu_T$ .

$\mu_T$  = total ionic strength.

$\mu_x$  = ionic strength of the electrolyte forming the solid phase of the mixture. (Saturating electrolyte).

$v_1$  = number of + ions from the saturating electrolyte.

$v_2$  = number of - ions from the saturating electrolyte.

$v_3$  = number of common ions from the added electrolyte.

$\mu$  = ionic strength factor.

$\mu_0$  = ionic strength of a saturated solution of the saturating electrolyte in pure water.

$\delta\mu_0(s)$  = activity coefficient of the standard electrolyte in a pure water solution at the ionic strength  $\mu_0$ .

The equation holds for homo-ions only, and for hetero-ions the equation becomes

$$\log \delta\mu_T(s) + k_1\mu_T + k_2(\mu_T - \mu_x) + \log \mu_x = \quad (8)$$

$$\log \delta\mu_0(s) + k_1\mu_0 + \log \mu_0.$$

Where the symbols have the same significance as in equation (7).

They illustrated the use of equation (7) with the two common ion pair KCl and HCl in  $H_2O$  and also with KCl and  $CoCl_2$  in water.

O'Brien<sup>3</sup> applied this equation to the various common ion combinations possible in the reciprocal salt pair, KCl,  $NaNO_3$  and  $H_2O$ . He found that the equation held for that system.

Previously O'Brien<sup>4</sup> measured and determined the solubility of KCl in solutions of varying concentrations of  $NaNO_3$ , no consideration being taken of the solid phase, it being tacitly assumed that it remained  $NaNO_3$  throughout. Reconsideration of the data of O'Brien in connection with the data of Uyeda<sup>5</sup> and Rienders<sup>6</sup> according to the method of Jänecke<sup>7</sup> has shown that beyond a  $NaNO_3$  concentration of about 2.5 M, (as shown in Fig. I) the solid phase changes from KCl to a mixture of KCl and  $KNO_3$ . Consequently the measurements of O'Brien that go beyond molality of 2.5 M do not represent KCl concentration but simply chloride concentration. Therefore in order to test the applicability of equation (8) for hetero-ionic pairs, it was decided to supplement the measurements of O'Brien by making the measurements of the solubility of KCl in the presence of  $NaNO_3$ , the concentration of the latter ranging from 0 to 2.5 M. Also O'Brien has found the relationship existing between the activity coeffi-

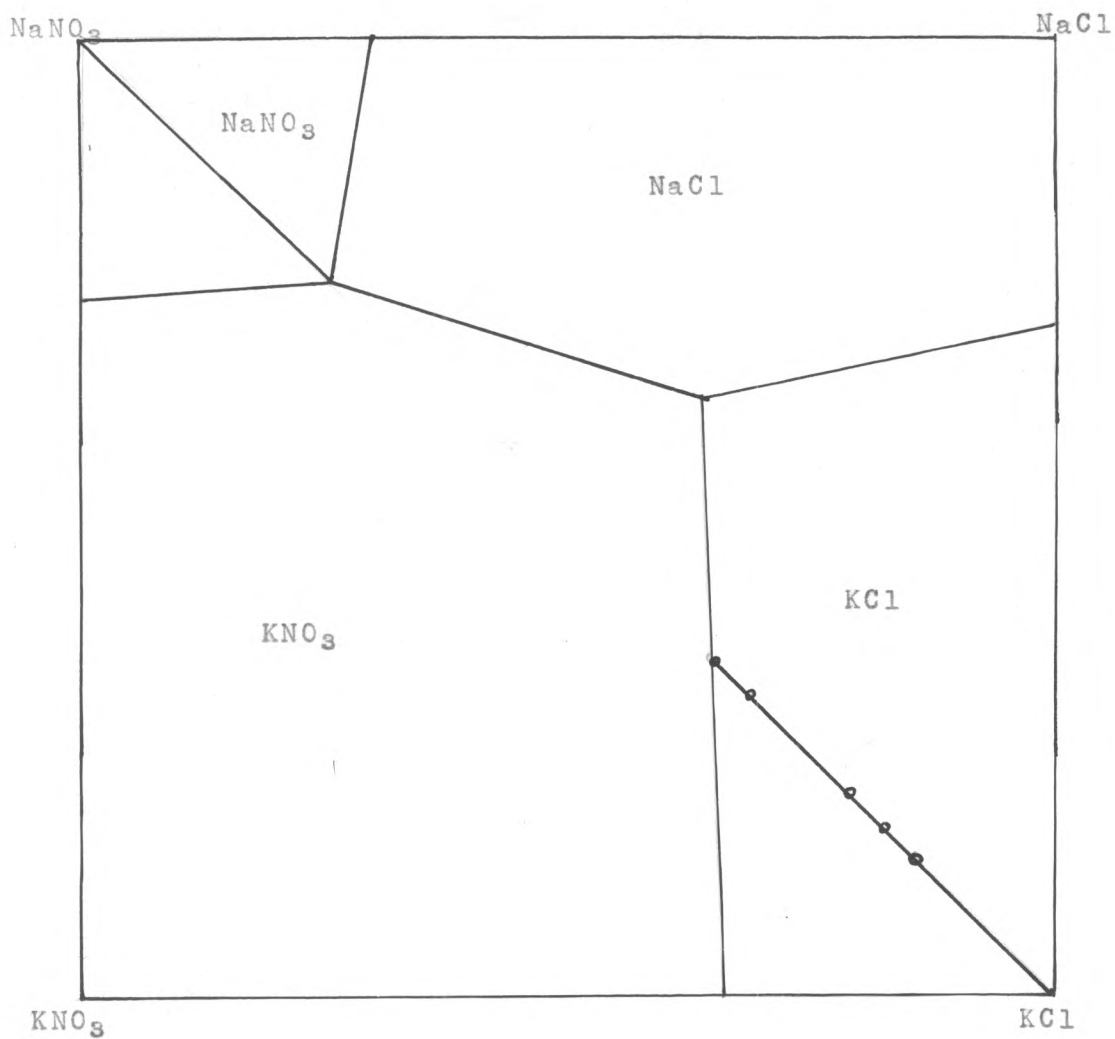


Fig. I: Equilibrium Diagram for the Reciprocal Salt Pair KCl and NaNO<sub>3</sub> at 25<sup>0</sup> C.

cient of an electrolyte in a mixture of electrolytes and the total ionic strength of the mixture which can be given by the equation

$$\log \gamma_{\mu_x} / \delta \mu_{T(S)} = k_3 \mu_T \quad (9)$$

which is represented graphically for KCl in NaNO<sub>3</sub> in Fig. II.

This equation in turn simplifies equation (7) and (8) of Akerlöf and Thomas, so that they become

$$\begin{aligned} \gamma_{\mu_{T(S)}} + k_3 \mu_T + v_1 / v_1 + v_2 \log \left[ v_3 (\mu_T - \mu_x) / n + v_1 \mu_x / n \right. \\ \left. + v_2 / v_1 + v_2 \log \mu_x / n \right] = \log \delta \mu_{O(S)} + k_1 \mu_O + \log \mu_O \end{aligned} \quad (10)$$

and

$$\log \gamma_{\mu_{T(S)}} + k_3 \mu_T + \log \mu_x = \log \delta \mu_{O(S)} + k_1 \mu_O + \log \mu_O. \quad (11)$$

In this paper equation (11) is tested by means of the system KCl, NaNO<sub>3</sub> and H<sub>2</sub>O.

## 2. Experimental

Material. Potassium Chloride. The highest grade Analytical Reagent chemical was used. It was recrystallized from conductivity water.

Sodium Nitrate. This was of high grade C.P. variety, free from chlorides as shown with AgNO<sub>3</sub>.

Silver Nitrate. For the analysis of the saturated solutions a N solution was made up with C.P. silver ni-

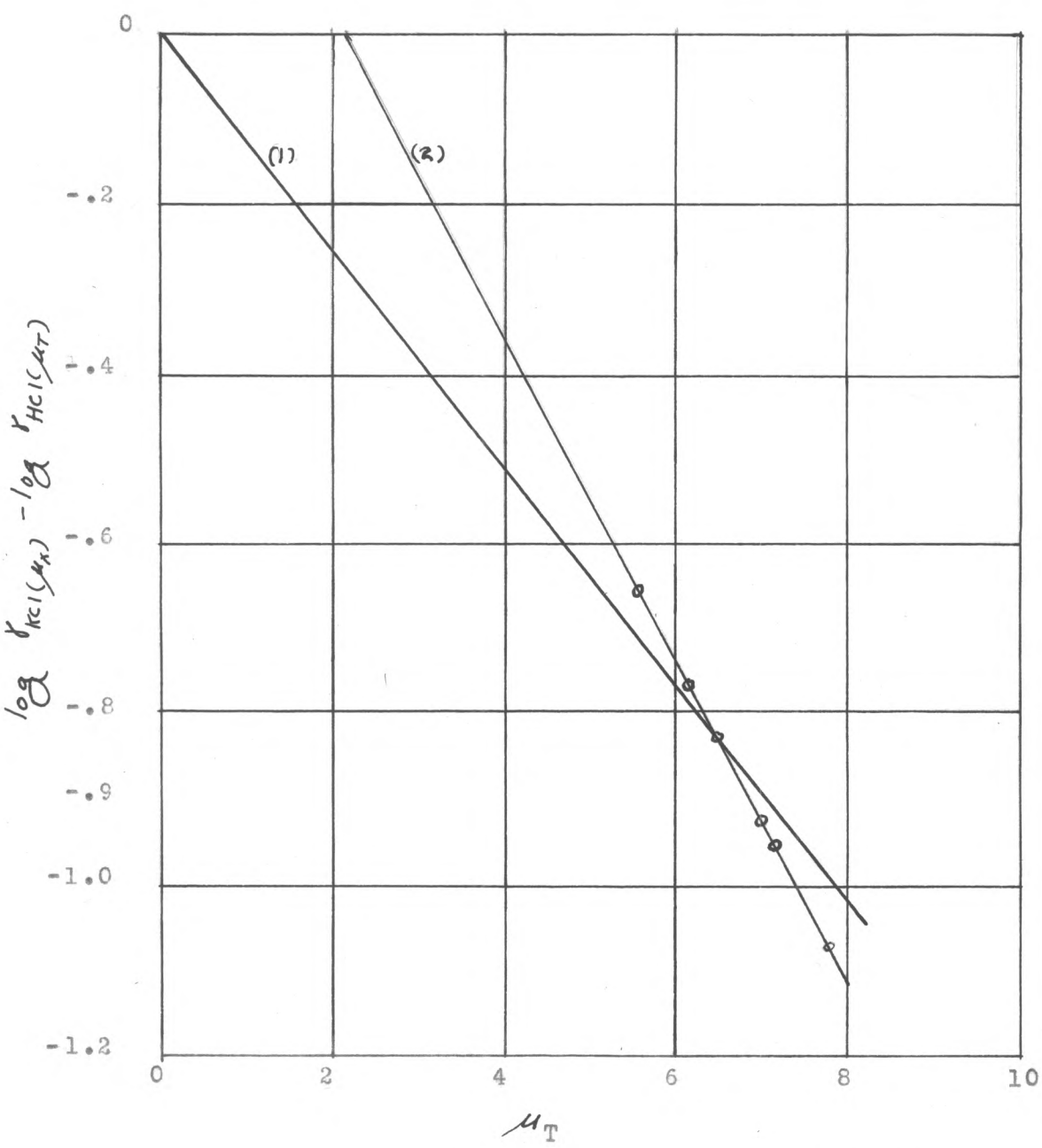


Fig. II: Activity Coefficients in Mixtures of Electrolytes.

1.  $\log \delta_{\mu_x} / \delta_{\mu_T} = k_3 \mu_T$

2.  $\log \delta_{\mu_x} / \delta_{\mu_T} = k_3 \mu_T + k_4$

trate. It was standardized against recrystallized potassium chloride.

Procedure. For the solubility determinations the method of Moody and Leyson<sup>8</sup> was used. Weighed amounts of sodium nitrate, potassium chloride and water were put in small tightly stoppered bottles, and placed in a water bath at about 40<sup>o</sup> C. These were then placed in a constant temperature bath at 25<sup>o</sup> C.  $\pm 0.1^{\circ}$ , and stirred automatically for an hour. It was found that longer stirring made no significant difference in the results and it was therefore concluded that an hour was sufficient for saturation.

Samples weighing 10 to 12 grams were siphoned through a filter; clear, colorless solutions being obtained. The sample was then analyzed for potassium chloride by the silver chromate method<sup>9</sup>. The solubility of KCl in pure water was taken to be 4.81 moles per 1000 g of water.<sup>10</sup>

### 3. Results

Table I: The Solubility of Potassium Chloride in the Presence of Sodium Nitrate at 25<sup>o</sup> C.

$M_T$	$M_O$	$M_x$	Dtns	Avg. Difference
5.47	0.50	4.97	2	$\pm 0.00$
6.09	1.00	5.09	2	$\pm 0.00$
6.59	1.41	5.18	3	$\pm 0.01$
7.14	1.84	5.30	3	$\pm 0.01$
7.32	2.00	5.32	2	$\pm 0.01$
7.93	2.50	5.43	4	$\pm 0.02$

Table I contains a summary of the data obtained. The first column ( $M_0$ ) gives the concentration of sodium nitrate in moles per 1000 grams of water. The second gives the number of determinations made. The third ( $M_x$ ) gives the solubility of potassium chloride, also expressed per 1000 grams of water, and the fourth gives the average error of measurements.  $M_T$  is the total molality of the mixture. This data is shown graphically in Fig. III.

#### 4. Calculation of Solubility

In applying the equation of Akerlöf and Thomas to these results, equation (8) is used which becomes

$$\log \delta \mu_{T(\text{HCl})} + k_1 \mu_T + k_2 (\mu_T - \mu_x) + \log \mu_x = .4681 \quad (12)$$

where both electrolytes are univalent. The constant  $k_2$  is calculated from this data as shown in Table II.

Table II: Constants for Equation (12).

$\mu_T$	$\mu_x$	$\log \delta \mu_{T(\text{HCl})}$	$k_2$
5.47	4.97	.4377	.0470
6.09	5.09	.5199	.0399
6.59	5.18	.5884	.0404
7.14	5.30	.6585	.0393
7.32	5.32	.6820	.0385
7.93	5.43	.7614	.0368
			mean .0403

In the above table  $\mu_T$  = total ionic strength of the mixture  $\text{NaNO}_3$  and  $\text{KCl}$ ;  $\mu_x$  = ionic strength of the

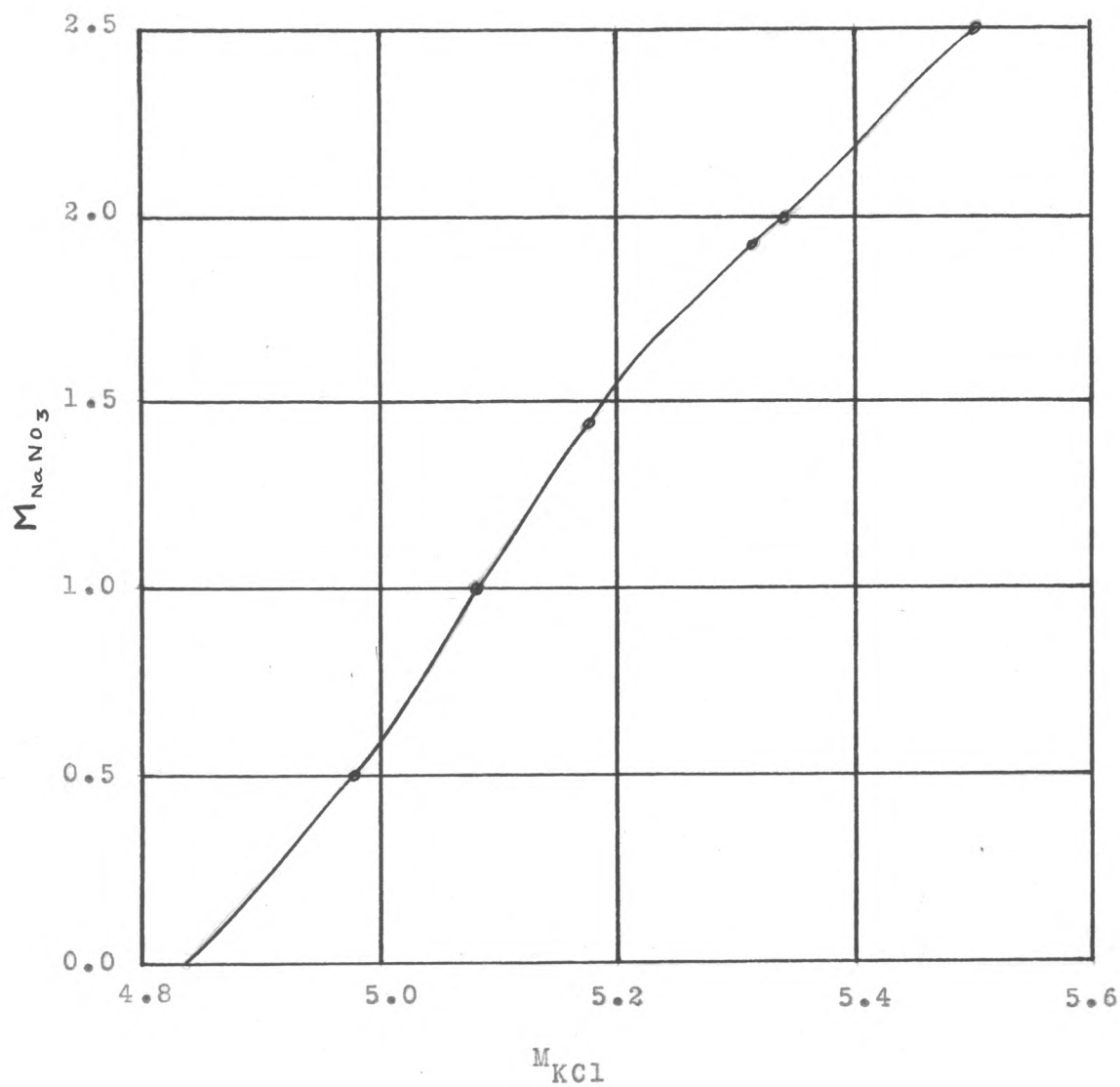


Fig. III: Solubility of  $\text{KCl}$  in  $\text{NaNO}_3$  at  $25^\circ\text{C}$ .

KCl in the mixture;  $k_2$  = the constant in equation (12).

The constant  $k_3$  in equation (11) was also calculated from the above data and was found to be  $.127 \pm 0.005$ . This constant was of no value as may be seen from Table III.

Table III: Solubility of KCl in  $\text{NaNO}_3$  as Calculated from Equation (11).

m $\text{NaNO}_3$	m KCl (obs.)	m KCl (calc.)
0.50	4.97	5.37
1.00	5.09	5.26
1.41	5.18	5.17
1.84	5.30	5.17
2.00	5.32	5.20
2.50	5.43	5.17

The explanation for this deviation may be seen in Fig. II (1). Only one of these points fall on the line, the slope of which is  $.127$  or  $k_3$ . If in Fig. II (2), when a line was drawn which passed through most of the points, it did not pass through the origin.

Therefore equation (11) becomes

$$\log \frac{\delta \mu_{T(S)}}{\mu_{T(S)}} + k_3 \mu_T + k_4 + \log \mu_x = \log \frac{\delta \mu_{O(S)}}{\mu_{O(S)}} + k_1 \mu_0 + \log \mu_0. \quad (13)$$

$k_3$  was now found to be  $-0.143 \pm 0.018$  and  $k_4$   $0.1054 \pm 0.005$ .

This is represented graphically in Fig. II (2).

Table IV: The Solubility of KCl in NaNO<sub>3</sub> as Calculated from Equations (8) and (13).

<sup>1</sup> m NaNO <sub>3</sub>	mKCl (obs.)	mKCl (eq.(8))	mKCl (eq.(13))
0.50	4.97	4.97	4.99
1.00	5.09	5.09	5.12
1.41	4.18	5.18	5.20
1.84	5.30	5.32	5.31
2.00	5.32	5.36	5.34
2.50	5.43	5.49	5.44

<sup>1</sup>  
m represents molality.

These results are shown graphically in Fig. IV.

### 5. Discussion of Results

In the calculation of the composition of a three component system it can be readily noted that the equations of Akerl<sup>o</sup>f and Thomas and the modified equation of O'Brien give results agreeing very closely with the experiment. It should be noted, however, that the reciprocal salt pair like the one considered in this paper is really a five and not a three component system. It does happen, though, that in such a system there are certain ranges of composition and concentration over which the system may be considered as consisting of just one pair of heteroionic salts. This of course presents a limitation to the value of the equation, since in order to apply the equation, the concentrations over which the equation will hold must be known. Further-

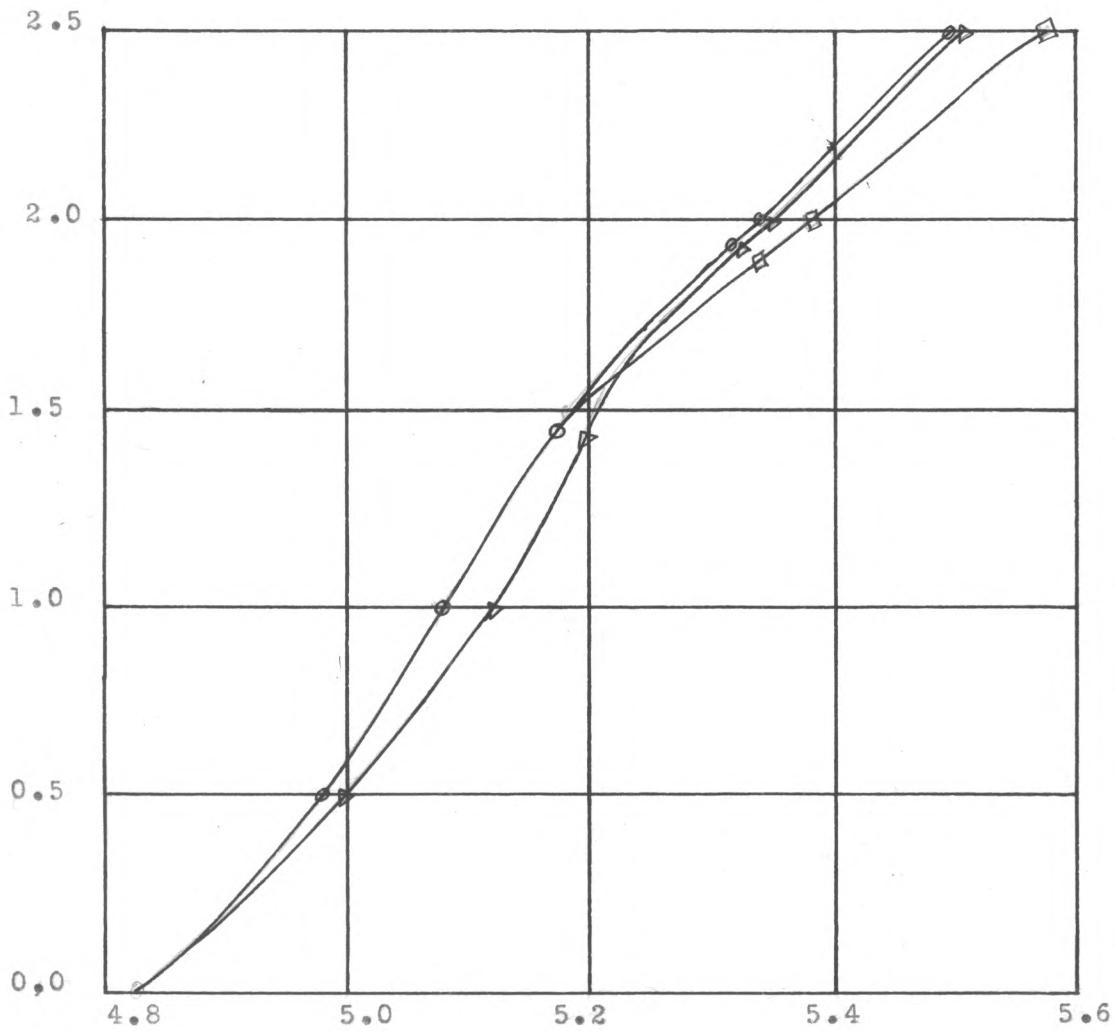


Fig. IV: Observed and Calculated Solubility  
of KCl in NaNO<sub>3</sub> at 25<sup>o</sup> C.

O = observed values.

Δ = O'Brien's equation.

□ = Akerlöf-Thomas equation.

more, the various constants for each different pair of electrolytes are different, and the constants also change for the same pair of electrolytes if the solid phase changes. In short, to apply the equation, the range of concentration over which the system might be considered as a three component system, the qualitative composition of the three phase system, and the solid phase of the system must be known. The equation is not adopted to a case where more than one electrolyte is present in the solid phase.

Of the two equations which are useful that of O'Brien is the more easily solved since it reduces to an equation of the form

$$\log x = A$$

for any given pair of univalent electrolytes and at any given ionic strength, while that of Akerl<sup>o</sup> and Thomas reduces to an equation of the form

$$\log x = B + Cx.$$

## 6. Summary

The solubility of KCl in NaNO<sub>3</sub> was measured over the nitrate concentration range 0 to 2.5 M.

The constants for the equations were determined.

The solubility of KCl was calculated from the equations using these constants.

Both equations hold very well (within limits) and O'Brien's is to be preferred since it is much easier to solve.

## 7. Literature Cited

- (1) Harned, Taylor's Treatise of Physical Chemistry,  
D. Van Nostrand and Co., 2nd Ed., (1931) Vol. I.,  
pp. 793-794.
- (2) Akerlöf and Thomas, J. Am. Chem. Soc., 56, 593 (1934).
- (3) O'Brien, Creighton University, unpublished.
- (4) O'Brien, Master's Thesis, Creighton University, (1933).
- (5) K. Uyeda, Mem. Coll. Sci. Kyoto 2, 245-9, (1910).
- (6) Reinders, Z. anorg. allg. Chem., 93, 202 (1915).
- (7) Janecke, Z. anorg. chem., 71 1 (1911).
- (8) Scott, Standard Methods of Chemical Analysis, D. Van  
Nostrand Co., 4th Ed., (1925), Vol. II, pp. 470-1.
- (9) Ibid., Vol. I., p. 150.
- (10) International Critical Tables, McGraw-Hill Co.,  
(1928) Vol., IV, p. 239.  
F. Klotman, Z. anal. Chem. 73, I (1928).  
O'Brien, Master's Thesis, Creighton University,  
(1933).