UNCLASSIFIED

ORNL 247
CHEMISTRY-GENERAL

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0360388 4

CHEMISTRY DIVISION

THE APPLICATION OF KINETIC THEORY TO THE CRITICAL CURVE FOR AQUEOUS SOLUTIONS OF 1-1 ELECTROLYTES

C.H. SECOY

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
CIRCULATION SECTION
4500N ROOM 175
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this report, send in name with report and the library will arrange a loan.
UCN-7969 (3 9-77)

OAK RIDGE NATIONAL LABORATORY

OPERATED BY
CARBIDE AND CARBON CHEMICALS CORPORATION
FOR THE
ATOMIC ENERGY COMMISSION
POST OFFICE BOX P
OAK RIDGE, TENNESSEE

UNCLASSIFIED

UNCLASSIFIED

ORNL-247

This document consists of 14 pages. This is Copy 7 of 110, Series A.

Issued to: _____

Contract No. W-7405, eng 26

CHEMISTRY DIVISION

THE APPLICATION OF KINETIC THEORY TO THE CRITICAL CURVE FOR AQUEOUS SOLUTIONS OF 1-1 ELECTROLYTES

C. H. SECOY

DATE ISSUED
JUL 27 1949

OAK RIDGE NATIONAL LABORATORY

Operated by
Carbide and Carbon Chemicals Corporation
for the
Atomic Energy Commission
Post Office Box P
Oak Ridge, Tennessee

UNCLASSIFIED

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0360388 4

ORNL 247
Chemistry-General

OAK RIDGE NATIONAL LABORATORY INTERNAL DISTRIBUTION:

1. G. T. Felbeck (C&CCC)
2. 706-A Library
3. 706-A Library
4. 706-B Library
5. Biology Library
6. Health Physics Library
7. Training School Library
8. Training School Library
9. Central Files
10. Central Files
11. Central Files
12. Central Files
13. J. A. Swartout
14. J. H. Gillette
15. F. L. Steahly
16. A. Hollaender
17. J. H. Frye, Jr.
18. E. J. Murphy
19. M. D. Peterson
20. C. N. Rucker
21. W. D. Lavers
22. A. M. Weinberg
23. J. A. Lane
24. C. H. Secoy
25. G. H. Jenks

OAK RIDGE NATIONAL LABORATORY EXTERNAL DISTRIBUTION:

26-33. Argonne National Laboratory
34. Armed Forces Special Weapons Project
35-36. Atomic Energy Commission, Washington
37. Battelle Memorial Institute
38-41. Brookhaven National Laboratory
42. Bureau of Ships
43-46. Carbide & Carbon Chemicals Corporation (K-25 Plant)
47-50. Carbide & Carbon Chemicals Corporation (Y-12 Plant)
51. Columbia University (Failla)
52. Dow Chemical Company
53-58. General Electric Company, Richland
59. Hanford Operations Office
60. Iowa State College
61-62. Kellex Corporation
63-66. Knolls Atomic Power Laboratory
67-69. Los Alamos
70. Massachusetts Institute of Technology (Gaudin)
71. Massachusetts Institute of Technology (Kaufmann)
72-74. Mound Laboratory
75. National Advisory Committee for Aeronautics
76-77. National Bureau of Standards
78. Naval Radiological Defense Laboratory
79. NEPA Project
80. New Brunswick Laboratory
81-82. New York Operations Office
83. North American Aviation, Inc.
84. Patent Branch, Washington
85. Sylvania Electric Products, Inc.
86-100. Technical Information Branch, ORE
101. UCLA Medical Research Laboratory (Warren)
102-105. University of California Radiation Laboratory
106-107. University of Rochester
108. Western Reserve University (Friedell)
109-110. Westinghouse Electric Corporation

THE APPLICATION OF KINETIC THEORY TO THE CRITICAL CURVE FOR AQUEOUS SOLUTIONS OF 1-1 ELECTROLYTES

by C. H. Secoy

Oak Ridge National Laboratory *

Oak Ridge, Tennessee

Even though extensive studies of the critical behavior of aqueous solutions have not been made, a sufficient number of qualitative observations and some quantitative measurements are available to permit a degree of generalization. As pointed out by Schröer[1], four basic types of temperature-composition diagrams are possible. In type I, the critical curve always lies in the region of unsaturated solutions. Even though the solubility continues to increase with temperature, the solubility curve never intersects the critical curve. In type II, the solubility curve reaches zero solubility at or below the critical temperature of the pure solvent. In this case the solute separates completely as either a solid phase or a second liquid phase, and the only critical phenomenon observed is that of the pure solvent. Types III and IV involve single and double intersections of the solubility curve and the critical curve.

With respect to aqueous solutions of electrolytes examples of types I, II and IV (single intersection) have been reported. Many salts undergo decomposition or irreversible hydrolysis at lower temperatures and do not permit their inclusion in such a classification. One-one electrolytes, insofar as they have been studied, all behave as type I. These include NaCl, KCl, RbCl, NaBr, KBr, NaI, KI, NH_4Cl and KNO_3[1], [2]. Examples of type II behavior are Na_2SO_4, K_2SO_4, $MgSO_4$[1] and UO_2SO_4[2].

*This document is based on work performed under Contract Number W-7405 eng 26 for the Atomic Energy Project at Oak Ridge National Laboratory.

Schröer[1] reported quantitative data for the elevation of the critical temperature as a function of concentration for NaCl, KCl, KBr, and KI. He found that his results could be expressed by an equation of the type, $\Delta T = kX^{1/n}$, in which n and k are constants for each salt, X is the concentration in moles per liter, and ΔT is the elevation of the critical temperature above that for water. Due to the similarity in form between this equation and the Freundlich adsorption isotherm, Schröer, in very general terms, attempted to explain his results on the basis of physical adsorption of water molecules on solute molecules as centers. Since the Freundlich isotherm is purely an empirical equation, and since the similarity in the equations is only a matter of form and does not hold if terms are compared, Schröer's explanation is at best only empirical and the agreement of the data with an equation of this type may well be only a fortuitous circumstance. In order to apply additional test to Schröer's adsorption concept, the Langmuir equation, the BET equation, and the Hüttig equation were applied in succession to his data. In no case was a reasonable curve obtained. It seems unlikely, therefore, that further thought in this direction can lead to anything more than the empirical description of the data which Schröer obtained. It is the purpose of this paper to demonstrate that the data can be fitted equally well to an equation derived directly from kinetic theory and in which the constants employed have a physical significance. In spite of the fact that a number of crude approximations for unknown quantities are made, the resulting relationship not only describes the data adequately, but also leads to values for inter-particle forces which are of the right order of magnitude and in the expected order.

Theoretical Part: There are several equations of state which more or less accurately describe the behavior of a pure substance in the vicinity of the

critical point. Such an equation should be of the third order in V and should involve not more than three constants. Van der Waals' equation and Dietericis equation as well as the Virial equation involving the second and third Virial coefficients all meet these requirements and we might choose any of these for our purpose. The conditions for criticality are that $\left(\frac{\partial P}{\partial V}\right)_T = 0$ and that $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$ and, if one applies these conditions to any one of the equations of state, an expression for T_c in terms of the equation constants can be obtained. We shall choose Van der Waals' equation for the following development, the choice being purely arbitrary since the argument advanced could be equally well applied to either of the others, and the results would be equally satisfactory.

Van der Waals' equation gives $T_c = \frac{a}{3.375\ Rb}$. (1)

Even though a and b are normally treated as constants, it is a well known fact that neither is constant for any known gas. The value of a is associated with the forces existing between molecules, and one would expect these forces to be dependent on temperature, and they would certainly be altered by the introduction of a second component. The value of b is related to the volume of the molecules themselves and is found to be slightly temperature-dependent. Furthermore, the introduction of a second component would alter b due to the presence of particles of a different size. We shall proceed to write expressions for a and b as functions of temperature and composition and, by substituting these expressions in equation (1), arrive at an equation for the critical temperature of a binary system.

It has been shown[3] that an expression representing intermolecular interaction in a binary mixture can be written as a quadratic function of the molecular concentrations. If we assume the solution in question is composed of simple water molecules, a positive ion, and a negative ion, the expression

becomes,

$$a = \gamma_1^2 a_{11} + 2\gamma_1\gamma_2 a_{12} + 2\gamma_1\gamma_3 a_{13} + \gamma_2^2 a_{22} + 2\gamma_2\gamma_3 a_{23} + \gamma_2^2 a_{33} \tag{2}$$

The γ's represent mole fractions, subscript one indicating water, subscript two the positive ion, and subscript three the negative ion. Three-particle interaction is neglected. The mole fractions can be expressed so that $\gamma_2 = \gamma_3$ and $\gamma_1 + 2\gamma_2 = 1$. Substituting γ_2 for γ_3 in expression (2), eliminating γ_1, and collecting terms we have,

$$a = a_{11} + k_1\gamma_2 + k_2\gamma_2^2 \tag{3}$$

where,

$$k_1 = 2a_{12} - 4a_{11} + 2a_{13} \tag{4}$$

and,

$$k_2 = 4a_{11} - 4a_{12} - 4a_{13} + a_{22} + 2a_{23} + a_{33} \tag{5}$$

Each of the a's is temperature dependent and each undoubtedly follows a different law of dependence. If one assumes a spherically symmetrical field, employs Boltzmann distribution for the potential energy function ω, and neglects all except binary encounters, a is given by an expression of the type,

$$a_{ij} = 2\pi NRT \int_{r_0}^{\infty} r^2 \left(1 - e^{-\frac{\omega_{ij}}{kT}}\right) dr. \tag{6}$$

Assuming the mutual potential energy, ω, is proportional to $1/r^s$ and introducing the function $X = r^s T$, the equation becomes,

$$a_{ij} = \frac{2\pi}{s} NRT^{1 - 3/s} \int_{r_0}^{\infty} X^{\frac{3}{s} - 1} \left(1 - e^{-\frac{\sigma}{X}}\right) dX \tag{7}$$

When the conditions for convergence of the integral quantity are met, this quantity will have a definite numerical value and we can then write, $a_{ij} \propto T^{1 - \frac{3}{s}}$. Each of the a's should, therefore, be proportional to some power of T. Since it is impossible with our present knowledge to write explicitly this order of dependence for each of the a's, we will make the crude assumption that the overall temperature dependence of a can be written as a single constant power of T and write for our final expression,

$$a = T^{\alpha}\left(a_{11} + k_1\gamma_2 + k_2\gamma_2^{\,2}\right) \tag{8}$$

Admittedly, this expression cannot be correct, since one would certainly not expect the same temperature dependence for the interaction between two water molecules as that for the interaction between an ion and a water molecule or between two ions. However, in view of our inability to do better without introducing an excessive number of unknown constants, we will test equation (8) with the available data. Certainly, if equation (8) satisfies the data, a more general expression would also be satisfactory.

The quantity b can be most simply represented as being proportional to the incompressible volume of particles in the system. In our case we can write,

$$b = k_3\left(r_1^{\,3}\gamma_1 + r_2^{\,3}\gamma_2 + r_3^{\,3}\gamma_3\right) \tag{9}$$

where k_3 includes the proportionality constant and the factor $4/3\,\pi$ from the volume expression for spheres of radii r_1, r_2 and r_3. The temperature dependence of b can be taken care of by introducing a factor, T^{β}. Eliminating γ_1 and γ_3 as before we have

$$b = k_3 T^{\beta}\left[r_1^{\,3} + \left(r_2^{\,3} + r_3^{\,3} - r_1^{\,3}\right)\gamma_2\right] \tag{10}$$

Combining equations (1), (8) and (10) and rearranging, we get,

$$T^n = \frac{a_{11} + k_1\gamma_2 + k_2\gamma_2^2}{3.375\ R\ k_3\left[r_1^3 + (r_2^3 + r_3^3 - r_1^3)\gamma_2\right]} \tag{11}$$

in which $n = 1 + \beta - \alpha$. This is the equation which we will apply to the data of Schröer and data obtained in this laboratory. It is obvious that data which gives a straight line on a log-log plot, as Schröer found that his did, can be described by an equation of the form of equation (11) by the proper selection of values for the constants involved.

Application to the Data: In order to use equation (11) it is first necessary to make some assumptions for the values of the radii of the interacting particles in the solution. Since the salts we are discussing are known to be completely ionic in character, we shall assume the salts to be completely ionized. However, in view of the fact that G. E. Owen[4] has reported the conductivity of dilute NaCl solution to be low in the critical region, we shall also assume that the ions carry with them essentially a monolayer of adsorbed water molecules. If the van der Waals radius is used for the water molecule, 1.06Å, this adsorbed layer increases the radius of a positive ion by 1.82 Å and that of a negative ion by 1.50 Å. The different effect on the two kinds of ions is due to the orientation of the H_2O dipole. These values combined with the known radii for the ions involved give the values listed in Table I. It should be emphasized that these values represent only one of many assumptions that one might make regarding the particles present and their effective size in the critical fluid, and success in applying equation (11) does not by any means substantiate their correctness. Since there is practically no proven knowledge concerning such a system, the assumptions made seem to be a reasonable initial step, and they remain to be

proven, disproven or altered in the light of new knowledge.

Table I

Selected Values for the Particle Radii

H_2O molecule	1.06 Å	Cl^- ion complex	3.31 Å
Na^+ ion complex	2.77	Br^- ion complex	3.45
K^+ ion complex	3.15	I^- ion complex	3.66

In the infinitely dilute solution, i.e., $\gamma_2 = 0$, equation (11) should reduce to the van der Waals' expression for T_c. It is obvious, therefore, that a_{11} is equal to the van der Waals a for water, 5.464 liters^2 x atm. per mole^2, and the quantity $k_3 r_1^3$ is equal to the van der Waals b, 0.03049 liters per mole. In this manner all quantities in equation (11) are given numerical value except the three constants, n, k_1, and k_2, and the variables T and γ. The simplified equations are the following:

For NaCl:
$$T^n = \frac{5.464 + k_1\gamma_2 + k_2\gamma_2^2}{0.008445 + 0.39941\ \gamma_2} \tag{12}$$

For KCl:
$$T^n = \frac{5.464 + k_1\gamma_2 + k_2\gamma_2^2}{0.008445 + 0.47038\ \gamma_2} \tag{13}$$

For KBr:
$$T^n = \frac{5.464 + k_1\gamma_2 + k_2\gamma_2^2}{0.008445 + 0.50439\ \gamma_2} \tag{14}$$

For KI:
$$T^n = \frac{5.464 + k_1\gamma_2 + k_2\gamma_2^2}{0.008445 + 0.56087\ \gamma_2} \tag{15}$$

If a set of experimental values for T and γ_2 for a given salt are available, (a minimum of three are required), the best values for n, k_1 and k_2 may be deter-

mined by the method of least squares or by solution of the simultaneous equations. In our case it was found less laborious to first eliminate k_1 and k_2 from the simultaneous equations and solve for n in the resulting equation by trial and error aided by graphical interpolation. Once the value of n was established, k_1 and k_2 were evaluated by least squares using all of the available data. In this manner the values given in table II were determined. The data which was used is given in the first two columns of table III, most of it being taken from Schröer's work. Schröer's data expressed concentrations in moles per liter, and, with the aid of the known densities for the salt solutions, these were converted to mole fractions. In calculating the mole fractions no correction for the combined water was made, even though this was the assumption of the model. Since we have no knowledge of the extent of such hydration, an accurate calculation cannot be made. If the hydration is of the order of one or two moles of water per ion, the correction would change the mole fractions only slightly and would not materially affect the results. However, if the degree of hydration were large, the values for the mole fractions would be altered considerably. Perhaps the fact that the equation applies as well as it does without this correction could be interpreted as evidence that the degree of hydration of the ions is not large.

Table II

Calculated Values of the Constants in Equations (12), (13), (14) and (15)

Solute	n	k_1	k_2
NaCl	0.999633	292.3	0
KCl	0.999740	348.2	-100
KBr	0.999349	364.8	500
KI	0.999509	402.9[5]	967

The third column of table III gives the calculated values for the critical temperature for comparison with the observed values. The average error between the values is 0.23°. The agreement is somewhat better than that found for the simple log-log plot used by Schröer.

The data from this laboratory were obtained by the same method as that used by Schröer, the apparatus differing in only minor details.

Table III

Calculated and Observed Critical Temperatures for Aqueous Salt Solutions

γ_2	T, °K observed	T, °K calculated	Difference
	NaCl		
0.000770(1)	651.26	651.52	+ 0.26
.001540(1)	654.01	654.29	+ 0.28
.003077(1)	658.71	659.33	+ 0.62
.006135(1)	667.81	667.66	- 0.15
.012193(1)	679.71	679.64	- 0.07
.015195(1)	683.86	684.10	+ 0.24
.02432	693.8	694.04	+ 0.24
	KCl		
0.000770(1)	651.91	651.92	+ 0.01
.001541(1)	655.71	655.44	- 0.27
.003081(1)	662.06	661.68	- 0.38
.006157(1)	671.26	671.62	+ 0.36
.012245(1)	685.36	684.94	- 0.42
.02618	700.3	700.20	- 0.10
	KBr		
0.000771(1)	652.66	653.12	+ 0.46
.001543(1)	656.06	656.32	+ 0.26
.003085(1)	662.41	662.15	- 0.26
.006169(1)	672.51	672.02	- 0.49
.02149	705.0	704.80	- 0.20
	KI		
0.000772(1)	652.61	652.58	- 0.03
.001544(1)	655.91	655.96	+ 0.05
.003091(1)	662.26	662.18	- 0.08
.006192(1)	673.16	673.08	- 0.08
.02363	717.8	717.82	+ 0.02
		Mean difference:	0.23

(1) Schröer's data

The Significance of the Constants: The fact that the values of n lie very close to unity shows that the temperature dependence of the van der Waals' constants is slight. This is qualitatively what one would expect since for one component system the variation of a and b with temperature is small, even in the critical region.

Values of k_1 and k_2 do not yield as much information as one would like, since each represents a combination of the different particle interactions. However, we can examine them in more detail. Let us look first at what happens to the equation as the mole fraction, γ_2, goes to higher values. In the case of NaCl the critical temperature would approach a nearly constant value of about 730° as γ_2 approaches 0.5. The curve for KCl actually goes through a maximum, and at $\gamma_2 = 0.5$ would have decreased to about 540°. For KBr and KI, however, due to large values for k_2 the temperature continues to rise to values of approximately 1700° and 2400°, respectively, at $\gamma_2 = 0.5$. It must be remembered that $\gamma_2 = 0.5$ does not indicate the pure anhydrous salt but represents the hypothetical substance composed of hydrated ions. If the degree of hydration of the ions decreases as the concentration of salt increases, the quantity in the denominator of equation (11) would decrease, and the critical temperatures would continue to rise to higher values than those indicated by the equation. That is to say, the radii of the particles involved must be a decreasing function of the concentration particularly in the more concentrated region.

Substituting values for k_1, k_2 and a_{11} into equations (4) and (5) and by combining these to eliminate common terms, we get,

$$(a_{K-K} - a_{Na-Na}) + 2(a_{K-Cl} - a_{Na-Cl}) = 11.8 \tag{16}$$

$$(a_{Br-Br} - a_{Cl-Cl}) + 2(a_{K-Br} - a_{K-Cl}) = 633.2 \tag{17}$$

$$(a_{I-I} - a_{Br-Br}) + 2(a_{K-I} - a_{K-Br}) = 543.3 \tag{18}$$

In these equations the subscripts indicate the hydrated ion particles for the mutual interaction involved. Looking at the last two equations, assuming that the quantity within each set of parentheses is a positive quantity, assigning positive signs to indicate repulsions and negative signs to indicate attractions, we get the following order for the magnitudes of the forces:

$$a_{I-I} > a_{Br-Br} > a_{Cl-Cl}$$

$$a_{K-Cl} > a_{K-Br} > a_{K-I}$$

These are precisely the orders in which the boiling points of the halogens and the alkali halides fall, and, in the case of the halogen gases, also the order of the critical temperatures. The same order would be expected for the critical temperatures of the potassium salts. However, if we apply the same reasoning to equation (16) the order is not that predicted from boiling points. For example, if we make a_{Na-Cl} less than a_{K-Cl} (the order of their boiling points) the quantity $(a_{K-Cl} - a_{Na-Cl})$ must be negative, and the quantity $(a_{K-K} - a_{Na-Na})$ must be positive. This makes $a_{K-K} > a_{Na-Na}$ which is the reverse of the order for the boiling points of the metals. Either the right hand member of equation (16) should be negative, which might well be without harming the applicability of equation (11) appreciably, or the comparison of the hydrated-ion substance with the anhydrous substances is not justified. The extrapolation of orders from boiling points to critical points may also not be justified.

Summary: An equation which gives the relation of critical temperature of aqueous solutions of 1-1 electrolytes to the composition of the solution has been developed by the application of kinetic theory. With the aid of assumptions concerning the types of particles present and their effective radii, this equation has been shown to describe the available data for solutions of NaCl, KCl, KBr,

and KI. The success in applying the equation does not substantiate the assumptions made but merely demonstrates the applicability of an equation based on kinetic theory. The significance of the numerical values obtained for the equation constants has been discussed.

REFERENCES

(1) Erich Schröer, Z. physik. Chem., 129, 79 (1927).

(2) C. H. Secoy, AECD-2265, (1948).

(3) E. H. Kennard, Kinetic Theory of Gases, pps. 221-237, McGraw-Hill Book Company, New York, N. Y., 1938. See also, Slater, Introduction to Chemical Physics, p. 194 ff, McGraw-Hill Book Company, New York, 1939.

(4) G. E. Owen, for Abstract see Phys. Rev., 75, 1303 (1949). Presented at the 1948 Annual Meeting of the American Physical Society, January 26-29, 1949, New York, N. Y.