

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

The Densities of Saturated Solutions of
NaCl and KCl from 10° to 105°C

by

V. L. Thurmond^{1/}, R. W. Potter II^{2/}, and M. A. Clynne

Open File Report

84-253

This report is preliminary and has not been reviewed
for conformity with U.S. Geological Survey editorial standards.

Any use of trade names is for descriptive purposes only
and does not imply endorsement by the USGS.

This study was supported by the Department of Energy under
Interagency Agreement DE-A197-79ET4461

^{1/} Present address: Rosenstiel School of Marine and Atmospheric
Science, University of Miami, 4600 Rickenbacker Causeway, Miami,
Florida 33149

^{2/} Present address: Occidental Research Corp., P. O. Box 19601,
Irvine, California 92713.

ABSTRACT

Experimental data and regression coefficients for equations describing the density of saturated NaCl and saturated KCl solutions in the temperature range 10-105°C are presented and compared with the available literature values. Data were obtained using calibrated hygrometers.

INTRODUCTION

The migration of fluid inclusions up thermal gradients in rock salt i.e., migration toward a waste canister, is potentially a serious problem with respect to the safe disposal of radioactive waste in mined salt repositories. In order to accurately predict the quantities of brine which will arrive at a waste canister during the thermal pulse, a quantitative model of the migration rate of brines as a function of the pertinent environmental parameters is needed. The basic equations for the migration of fluid inclusions in salt (Anthony and Cline, 1974; Bradshaw and Sanchez, 1969; Gaffney, 1978) have been derived assuming that diffusion is the dominant transport mechanism of NaCl across the inclusion. These models assume a saturated NaCl solution is the included fluid and require its density as an input parameter. The data base employed for the calculations is the set of densities for NaCl-H₂O saturated solutions measured by the Earl of Berkeley (1904). These data cover the range of 0° to 107°C and have been linearly extrapolated to 300°C for use in the migration calculations (Bradshaw and Sanchez, 1969). Recent studies indicate systematic departures between the NaCl solubility values obtained by the Earl of Berkeley and those which we measure (Potter and Clynne, 1978; Clynne and Potter, 1979). In view of the uncertainties in the existing literature data, in particular the systematic deviations of the Earl of Berkeley's numbers from our studies, and the need for an accurate data base for the migration equations, we have undertaken a study of the densities of saturated NaCl and saturated KCl solutions from 10° to 105°C.

EXPERIMENTAL METHOD

In this study, glass hydrometers which can be read to 0.0001 g/cm³ were used to measure specific gravity. The hydrometers were calibrated for use at 15.56°C. Hence, correction for the thermal expansion of the glass must be applied to measurements at other temperatures. The experimental apparatus is illustrated in Fig. 1, and the procedure used was as follows:

1. A saturated solution of reagent-grade salt was prepared in a 500 ml cylinder, with excess salt added to assure saturation.
2. A hydrometer and a thermometer were placed in the solution, and the assembly heated in the bath to the desired temperature.
3. The solution was stirred vigorously for several minutes to eliminate thermal and compositional gradients.
4. The specific gravity and temperature were read.
5. Steps 3 and 4 were repeated until constant values were measured.

For temperatures up to 100°C, a platinum resistance thermometer accurate to $\pm 0.02^\circ\text{C}$ and precise to $\pm 0.005^\circ\text{C}$ was used. At temperatures above 100°C, NBS mercury-in-glass thermometers which could be read to $\pm 0.01^\circ\text{C}$ were used.

Cylinders containing the salt solutions were immersed in a 25 liter pyrex tank filled with ethylene glycol. The temperature of the bath and the temperature of the solutions were monitored simultaneously with separate thermometers to assure thermal uniformity. The temperature of the bath was regulated to $\pm 0.01^\circ\text{C}$.

A hand-held electric stirrer was used to insure saturation of the solution after changes in temperature. Equilibrium between the salt and saturated solution was verified by additional stirring and rechecking the measurement. The entire series of measurements was repeated proceeding from high temperature to low temperature. Specific gravity measurements were converted to densities using the ASME steam tables.

To test the accuracy and precision of the experimental method, we measured the density of pure water over a range of temperatures. Of prime concern was the accuracy of the coefficient of thermal expansion ($2.5 \times 10^{-5} \text{ cm}^3/\text{cm}^3/^\circ\text{C}$) of the hydrometers. A comparison of measured values with those from the ASME steam tables (Table 1) showed that the two sets are in agreement within the respective tolerances. The mean deviation of our measured values from the pure water data is $\pm 0.8 \times 10^{-4} \text{ g/cm}^3$ while the precision of the experimental method is $\pm 1 \times 10^{-4} \text{ g/cm}^3$. The accuracy of the data is taken as $\pm 2.4 \times 10^{-4} \text{ g/cm}^3$; however, it should be noted that the method reproduced the international standard values for pure water within $\pm 2 \times 10^{-4} \text{ g/cm}^3$.

RESULTS

The experimental densities obtained for saturated NaCl and saturated KCl solutions are given in Tables 2 and 3 respectively. The values were fit to an equation of the following form:

$$\rho = \sum_{i=0} a_i t_i$$

where ρ is the density in g/cm^3 , t_i is the temperature in degrees Celsius, and a_i are empirical coefficients derived from least squares regression. The empirical coefficients and the mean deviation of the experimental data from a smooth curve are given in Table 4.

DISCUSSION OF RESULTS:

Table 5 compares the results of this study with results obtained by previous investigators. In general, the densities obtained in this study are greater than those of previous workers except those reported by Haas (1976). His values were obtained by correlating the available density data for unsaturated NaCl solutions and extrapolating to the NaCl saturation curve of Potter, Babcock, and Brown (1977). The deviation of the results reported here from those of Haas (1976),

Postnikov (1968), and Cornec and Krombach (1932) (except for the 108.5°C KCl value) are within the stated precision and accuracies of their values. The data of Blasdale (1918) appear to be discordant with the results of all the other workers. The values of Ingham (1928) and Volz-Fladrich (1962) deviate from our values by 3 to 4 times their stated precision. The systematic deviation of the Earl of Berkeley's (1904) values probably results from a systematic error in the water densities he used to calibrate his apparatus.

CONCLUSIONS:

The data set presented here appears to be the most reliable set available inasmuch as the experimental method reproduced the standard density values for pure water. The correlation of Haas (1976) for the density of saturated NaCl solutions from 80° to 325°C adequately represents the data for saturated NaCl solutions within its stated precision. From 10° to 85°C the data presented here (Table 6) should be employed in migration equations, while at $T > 85^{\circ}\text{C}$ it is recommended that the values of Haas (1976) be used for the migration equations rather than values extrapolated from the Earl of Berkeley's data set (Bradshaw and Sanchez, 1969). Using the new set of densities will yield migration rates which are a few tenths of a percent faster than those calculated by Bradshaw and Sanchez.

REFERENCES

- Anthony, T. R. and Cline, H. E., 1974, Thermomigration of liquid droplets in salt: Fourth Symposium on Salt, v. 1, A. H. Coogan Ed., p. 313-321. The Northern Ohio Geological Society, Inc., Cleveland, Ohio.
- Blasdale, W. C., 1918, Equilibria in solutions containing mixtures of salts. I. The system water and the sulfates and chlorides of sodium and potassium: *Journal of Industrial and Engineering Chemistry*, v. 10, p. 344-353.
- Bradshaw, R. L. and Sanchez, F., 1969, Migration of brine cavities in rock salt: *Journal of Geophysical Research*, v. 74, p. 4209-4212.
- Clynne, M. A. and Potter, R. W., II, 1979, The solubility of some alkali and alkaline earth chlorides in water at moderate temperatures: *Journal of Chemical Engineering Data*, v. 24, p. 338-340.
- Cornec, E. and Krumbach, H., 1932, Equilibres entre le chlorure de potassium, le chlorure de sodium et l'eau depuis -23° jusqu'à +190°: *Annales de Chimie*, v. 18, p. 5-23.
- Earl of Berkeley, 1904, On some physical constants of saturated solutions: *Royal Society of London Philosophical Transactions, Series A.*, v. 203, p. 189-215.
- Gaffney, E. S., 1978, Brine migration: Report # PT-U78-0242, Pacifica Technology, Del Mar, Calif., 24 p.
- Haas, J. L., Jr., 1976, Physical properties of the coexisting phases and thermochemical properties of the H₂O component in boiling NaCl solutions: *U.S. Geological Survey Bulletin* 1421-A, 73 p.
- Ingham, J. W., 1928, The apparent hydration of ions. Part I. The densities and viscosities of saturated solutions of sodium and potassium chlorides in hydrochloric acid: *Journal of the American Chemical Society*, v. 50, p. 1917-1930.
- Postnikov, V. A., 1968, Density and viscosity of saturated aqueous solutions of certain substances: *Zhurnal Prikladnoi Khimii*, v. 44, p. 236-238.
- Potter, R. W., II, Babcock, R. S., and Brown, D. L., 1977, A new method for determining the solubility of salts in aqueous solutions at elevated temperatures: *Journal of Research of the U. S. Geological Survey*, v. 5, p. 387-395.
- Potter, R. W., II and Clynne, M. A., 1978: Solubility of highly soluble salts in aqueous media - Part I. NaCl, KCl, CaCl₂, Na₂SO₄, and K₂SO₄ solubilities to 100°C: *Journal of Research of the U. S. Geological Survey*, v. 6, p. 701-705.
- Volz-Fladrich, H., 1962, Physical-chemical investigation of the systems MgCl₂-HCl-H₂O, NaCl-HCl-H₂O, and KCl-HCl-H₂O: *Freiberger Forschungshefte*, v. 134, p. 1-85.

Table 1. Comparison of the experimental values of pure water with the internationally accepted values from the ASME steam tables.

T°C	ρ measured g/cm ³	ρ ASME g/cm ³	$\Delta = \rho \text{ ASME} - \rho \text{ meas.}$ g/cm ³ x 10 ⁴
19.60	0.9983	0.9983	0
28.55	.9960	.9961	1
36.75	.9936	.9934	-2
43.70	.9908	.9908	0
50.17	.9880	.9880	0
58.77	.9837	.9838	1
68.73	.9785	.9784	-1
75.44	.9745	.9745	0
81.38	.9710	.9708	-2
89.49	.9655	.9656	1

Table 2. Experimental densities for saturated NaCl solutions and the deviations from the least-squares regression.

T°C	Experimental ρ g/cm ³	deviation g/cm ³ x 10 ⁴
14.02	1.2049	2
17.37	1.2031	-2
25.37	1.1998	0
33.02	1.1964	-1
40.97	1.1928	-2
47.46	1.1902	0
49.83	1.1891	-1
49.93	1.1892	1
56.11	1.1866	2
60.80	1.1846	2
60.86	1.1846	2
60.91	1.1846	2
68.24	1.1812	0
68.27	1.1811	-1
70.25	1.1801	-2
70.27	1.1801	-2
73.54	1.1791	2
78.85	1.1765	-2
88.27	1.1726	0
88.53	1.1725	0
96.4	1.1692	1
96.7	1.1689	-1
103.4	1.1662	1
103.7	1.1661	0

Table 5. Comparison of the equations derived from the experimental densities with the densities determined in previous studies. (Δ = observed - calculated)

NaCl			KCl		
Reference	T°C	$\Delta \times 10^4$ g/cm ³	Reference	T°C	$\Delta \times 10^4$ g/cm ³
Earl of Berkeley (1904)	0.35	-16	Earl of Berkeley (1904)	0.7	-10
"	15.20	-22	"	19.55	-9
"	30.05	-22	"	32.80	-11
"	45.40	-20	"	59.85	-12
"	61.70	-17	"	74.80	-13
"	75.65	-16	"	89.45	-21
"	90.50	-15	"	108.0	-30
"	107.0	-13	Blasdale (1918)	0	-41
Blasdale (1918)	0	-38	"	25	+57
"	25	-9	"	50	+2
"	50	-21	"	75	-46
"	75	+18	"	100	-2
"	100	+55	Ingham (1928)	25	-12
Ingham (1928)	25	-18	Cornec & Krombach (1932)	0	-1
Cornec & Krombach (1932)	0	-18	"	20	-11
"	20	-18	"	40	-5
"	40	-14	"	60	-2
"	60	-8	"	80	-11
"	80	-1	"	100	-31
"	100	-15	"	108.5	-60
"	108.7	-17	Volz-Fladrich (1962)	0	-5
Volz-Fladrich (1962)	0	-14	"	25	-14
"	25	-19	"	35	-14
"	35	-19	"	45	-15
"	45	-20	Postnikov (1968)	10	-6
Postnikov (1968)	20	-1	"	20	-21
"	30	+13	"	30	-10
"	40	-4	"	40	-15
"	50	-11	"	50	-8
"	60	+2	"	60	-2
"	70	-4	"	70	10
"	80	-1	"	80	21
Haas (1976)	80	+9			
"	85	+10			
"	90	+12			
"	95	+14			
"	100	+5			
"	105	+7			
"	110	-1			

Table 3. Experimental densities for saturated KCl solutions and the deviations from the least-squares regression.

T°C	Experimental ρ g/cm ³	deviation g/cm ³
13.15	1.1687	0
13.52	1.1692	1
23.35	1.1780	0
30.06	1.1831	0
36.88	1.1873	-2
44.99	1.1925	3
53.86	1.1965	0
61.96	1.2000	0
69.24	1.2026	-2
79.61	1.2061	-1
89.65	1.2090	3
98.8	1.2101	-2
103.3	1.2107	1
104.2	1.2108	0

Table 4. Coefficients for the least-squares regression of the experimental densities and the mean deviation of the data from a smooth curve

	a_0	a_1	a_2	a_3	a_4	$\mu_s \times 10^4$
NaCl	1.21088	-4.38857×10^{-4}	6.124017×10^{-8}			1.2
KCl	1.15301	1.3942×10^{-3}	-1.6718×10^{-5}	1.3514×10^{-7}	-4.997×10^{-10}	1.0

Note: These equations are valid from 10°C to 105°C and can not be extrapolated with any reliability.

Table 6. Smoothed values for the densities of saturated solutions of the respective salts.

T°C	ρ_{sat} NaCl g/cm ³	ρ_{sat} KCl g/cm ³
10	1.2065	1.1653
15	1.2043	1.1706
20	1.2021	1.1753
25	1.1999	1.1794
30	1.1978	1.1831
35	1.1956	1.1864
40	1.1934	1.1894
45	1.1913	1.1922
50	1.1891	1.1947
55	1.1869	1.1970
60	1.1848	1.1992
65	1.1826	1.2012
70	1.1805	1.2030
75	1.1783	1.2048
80	1.1762	1.2063
85	1.1736	1.2077
90	1.1719	1.2089
95	1.1697	1.2098
100	1.1676	1.2105
105	1.1655	1.2108

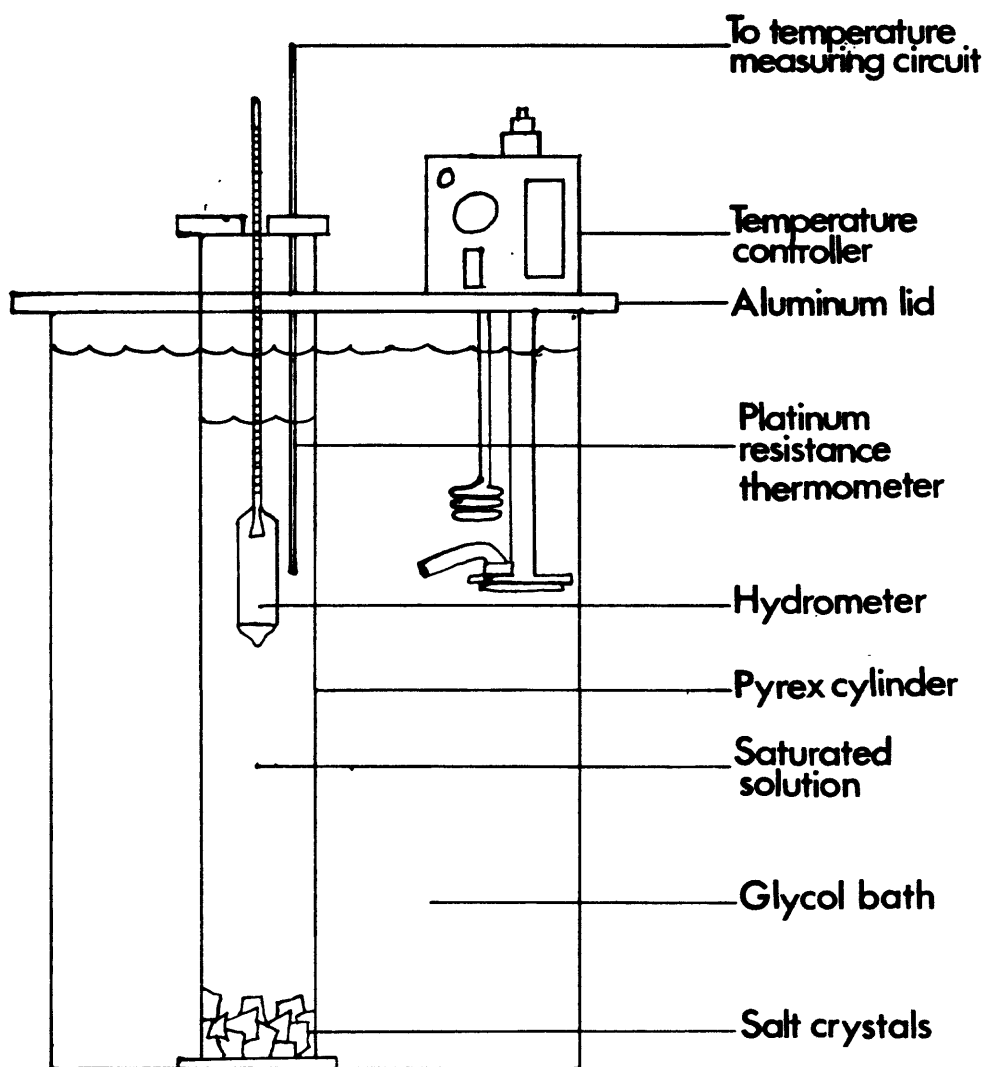


Figure 1. Schematic diagram of the experimental apparatus used in this investigation.