The Volumetric properties of vapor-saturated aqueous potassium hydroxide
solutions from 0° to 400°C & vapor-saturated aqueous solutions of aqueous
sodium hydroxide from 0° to 350°C based on a regression of the
available literature data
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Pressure-volume-temperature-composition (P-V-T-X) data for brines
are required to establish optimum operating conditions for the production
of geothermal brine fields; to minimize scaling and corrosion; and to
intelligently design turbines for production of electricity. Precise
thermodynamic data derived from the volumetric properties of the brines
are prerequisite for chemical and reservoir modelling of geothermal brine
systems. In view of the importance of P-V-T-X data to the utilization
and understanding of geothermal brine systems, a compilation of the available
literature data (Potter et al., 1975) and evaluations of these data for NaCl,
KCl, $CaCl_2$, Na_2SO_4, and K_2SO_4 have been completed (Potter and Brown, 1975,
1976a, 1976b, 1976c; Potter and Clynne, 1976).

Prior to this report, the only extensive tabulation of volumetric data
for aqueous, vapor-saturated potassium and sodium hydroxide solutions was
the International Critical Tables (National Research Council, 1928), in
which a compilation of density values is presented for aqueous potassium
hydroxide solutions for concentrations of 1 weight percent to 50 weight
percent from 0°C to 100°C. There are no compilations available for potassium
and sodium hydroxide solutions at pressures greater than the saturation vapor
pressure (Potter, 1976). The purpose of this report is to provide an internally
consistent set of density values for vapor-saturated, aqueous potassium hydroxide
solutions from 0°C to 400°C and for vapor-saturated, aqueous sodium hydroxide
solutions from 0°C to 350°C based on the currently available experimental data
summarized by Potter et al. (1975).

The density data presented in Tables 1, 2, 4, and 5 were obtained from
regression analysis of the P-V-T-X data taken from the International Critical

Tables (National Research Council, 1928) and the 43 references cited by Potter et al. (1975). The data summarized in tables 1 and 2 are for vapor-saturated potassium hydroxide solutions from 0°C to 400°C and the data in tables 4 and 5 are for vapor-saturated sodium hydroxide solutions from 0°C to 350°C. The regression was accomplished by using a linear least-squares polynomial fit method in which each data point was weighted with respect to its relative uncertainty. The uncertainties used were for the most part those assigned by the experimentalist. However, in those cases where uncertainties were not stated, an estimate was supplied on the basis of the experimental method employed in the study.

The experimental densities were fit at constant temperature as a function of composition for each solute. In most cases a simple polynomial equation relating either the density, d, and the molality, m, of the solution,

$$d = \sum_{j=1}^{n} B_j(t)m^j \; , \tag{1}$$

or the density and the square-root of the molality,

$$d = \sum_{j=1}^{n} C_j(t)m^{j/2} \; , \tag{2}$$

was used for regression purposes. However, it was found that converting the density data to apparent molal volume, ϕ_v, and then fitting this as a function of the square-root of molality resulted in a more accurate and economical (lower-order) representation of the data when very precise measurements were available. The equation used in this case is given by

$$\phi_v = \sum_{j=1}^{n} A_j(t)m^{j/2} \; . \tag{3}$$

The density can be calculated from the apparent molal volume by using the relation

$$d = \frac{1000 d_0 + M_2 m d_0}{1000 + \phi_v m d_0}$$ (4)

where M_2 is the molecular weight of the solute and d_0 is the density of water. In general the order, n, of the fitting polynomial was chosen such that the standard deviation of the resulting regression would represent the internal consistency of the data used in the fit.

Tables 3 and 6 summarize the coefficients of the equations used to generate the density tabulations given here, and may be used for interpolation to determine densities of solutions with concentrations other than those given in tables 1, 2, 4, and 5.

Because of the inadequate data base, it was not possible to generate a set of density values at pressures greater than the saturation vapor pressure for either potassium hydroxide or sodium hydroxide which would accurately represent the behavior of each solution above its saturation surface.

REFERENCES

International Critical Tables of Numerical Data, Physics, Chemistry and Technology, 1928, National Research Council: New York, McGraw-Hill Book Co., Inc., v. 3, 444 p.

Potter, R. W., II, 1976, An assessment of the status of the available data on the P-V-T properties for the major components in geothermal brines: Proceedings, Second U.N. Symposium on the Development and Use of Geothermal Resources, v. 1, pp. 827-829.

_____and Brown, D. L., 1975, The volumetric properties of aqueous sodium chloride solutions from 0° to 500°C at pressures up to 2000 bars based on a regression of the available literature data: U.S. Geol. Survey Open-file Report #75-636, 31 p.

_____1976a, The volumetric properties of vapor saturated aqueous potassium chloride solutions from 0° to 400°C based on a regression of the available literature data: U.S. Geol. Survey Open-file Report #76-243, 6 p.

_____1976b, The volumetric properties of vapor saturated aqueous sodium sulfate solutions from 0° to 325°C based on a regression of the available literature data: U.S. Geol. Survey Open-file Report #76-255, 6 p.

_____1976c, The volumetric properties of vapor saturated aqueous potassium sulfate solutions from 0° to 200°C based on a regression of the available literature data: U.S. Geol. Survey Open-file Report #76-501, 7 p.

Potter, R. W., II, and Clynne, M. A., 1976, The volumetric properties of vapor saturated aqueous calcium chloride solutions from 0° to 300°C based on a regression of the available literature data: U.S. Geol. Survey Open-file Report #76-365, 7 p.

Potter, R. W., II, Shaw, D. R., and Haas, J. L., 1975, Annotated bibliography of studies on the density and other volumetric properties for major components in geothermal waters 1928-74: U.S. Geol. Survey Bull. 1417, 78 p.

Table 2. Density of KOH Solutions (g/cm^3).

p(°C)	1	3	5	7	9	11	13	15	20	25	30	35	40	45	50	60	70	80	90	
								CONCENTRATION (WEIGHT PERCENT)												
	1.0095	1.0281	1.0450	1.0596	1.0711	1.0788	1.0819	1.0794	1.1954	1.2463	1.2984	1.3520	1.4075	1.4653	1.5256	--	--	--	--	±.0002
	1.0059	1.0238	1.0419	1.0602	1.0786	1.0973	1.1161	1.1352	1.1838	1.2338	1.2853	1.3386	1.3936	1.4505	1.5085	--	--	--	--	±.0002
	.9969	1.0144	1.0320	1.0498	1.0678	1.0860	1.1045	1.1233	1.1714	1.2211	1.2723	1.3250	1.3792	1.4353	1.4944	--	--	--	--	±.0004
	.983	1.000	1.017	1.034	1.052	1.070	1.088	1.107	1.155	1.205	1.256	1.310	1.364	1.420	--	--	--	--	--	±.0002
	.974	.989	1.005	1.022	1.038	1.056	1.073	1.091	1.137	1.186	1.237	1.290	1.344	1.400	1.456	1.567	--	--	--	±.0002
	.935	.948	.964	.981	.999	1.018	1.036	1.055	1.104	1.153	1.204	1.257	1.311	1.366	1.422	1.537	1.653	1.768	--	±.0002
	.873	.893	.914	.934	.954	.974	.994	1.014	1.064	1.115	1.166	1.220	1.274	1.330	1.387	1.503	1.620	1.730	1.850	±.0005
	.797	.826	.851	.875	.898	.920	.942	.964	1.018	1.071	1.125	1.180	1.235	1.292	1.350	1.467	1.583	1.692	1.800	±.0005
	.702	.742	.774	.803	.830	.856	.880	.905	.964	1.022	1.079	1.136	1.194	1.252	1.312	1.432	1.550	1.661	1.764	±.0005
	.600	.650	.689	.723	.754	.784	.812	.839	.905	.968	1.030	1.091	1.152	1.213	1.275	1.398	1.517	1.626	1.722	±.0005
	--	--	--	--	--	--	--	--	--	--	--	--	1.108	1.174	1.237	1.360	1.480	1.594	1.685	±.0005

Table 3. Interpolation Equation Coefficients for KOH Solutions.

The available density data for temperatures between $0°$ and $50°C$ were converted to apparent molal volumes and fit by the method of least squares to a polynomial equation of the form

$$\phi_v = \sum_{i=0}^{4} A_i m^{i/2},$$ where m is the molality of the solution.

Density may be calculated by using the formula

$$d = (1000d_0 + M_2 m d_0)/(1000 + \phi_v m d_0),$$

where $M_2 = 56.109$ g/mole and d_0 is the density of water. The interpolation equations are valid for concentrations up to 17.8 molal (50 wt%).

Temp. (°C)	A_0	A_1	A_2	A_3	A_4	d_0 (g/cm)
0	.4093	2.7870	1.8974	-.5835	.04833	.999840
25	6.3465	-.46054	2.6470	-.67788	.05523	.997047
50	5.0719	3.47176	-.04192	.03755	-.011032	.988038

For temperatures of 75° and 100°C, the available data were fit to a 3rd-order polynomial equation. The equation for 75°C solutions is valid for concentrations from 0 to 15.3 molal (0 to 46 wt%), while the equation for 100°C solutions is valid from 0 to 31 molal (0 to 64 wt%).

$$d = B_0 + B_1 m + B_2 m^2 + B_3 m^3$$

	B	$10 \times B_1$	$-10^2 \times B_2$	$10^4 \times B_3$
75	.97508	.4584	.1321	.1836
100	.96602	.4296	.1073	.1150

For temperatures from 150° to 400°C, the available data were fit to a 5th-order polynomial equation of the form

$$d = \sum_{j=0}^{5} C_j m^{j/2}$$

The range of concentrations for which these interpolation equations are valid vary, and are indicated in the table below with the coefficients:

Temp. (°C)	Range of validity (molality)	(wt%)	C_0	$10 \times C_1$	$10 \times C_2$	$-10 \times C_3$	$10^3 \times C_4$	$-10^4 \times C_5$
150	0-108	0-86	.94076	-.4846	.9064	.1748	1.3858	.40696
200	0-158	0-90	.86476	-.09157	.7429	.1407	1.048	.2822
250	0-158	0-90	.77552	.2633	.6487	.1283	.9678	.2624
300	0-158	0-90	.660828	.76101	.51670	.11013	.8440	.2299
350	0-158	0-90	.54334	1.1571	.45238	.10623	.8417	.2338
400	0-158	0-90	-.00875	5.1638	-.75017	-.066932	-.3504	-.07993

Table 4. Density of NaOH Solutions (g/cm³).

p.)	Concentration (Molality)																		
	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	22.5	25.0	
0	1.0240	1.0463	1.0674	1.0875	1.1067	1.1252	1.1430	1.1601	1.1766	1.1925	1.2641	1.3243	1.3750	1.4182	1.4551	1.4870	1.5150	1.5399	±.0003
5	1.01867	1.03928	1.0591	1.0782	1.0966	1.1144	1.1316	1.1482	1.1642	1.1797	1.2499	1.3092	1.3595	1.4023	1.4389	1.4704	1.4976	1.5210	±.0003
0	1.00891	1.02873	1.0478	1.0663	1.0842	1.1015	1.1183	1.1346	1.1504	1.1656	1.2351	1.2939	1.3434	1.3850	1.4204	1.4511	1.4785	1.5039	±.0006
0	.9984	1.0181	1.0371	1.0554	1.0731	1.0902	1.1068	1.1229	1.1384	1.1535	1.2220	1.2803	1.3297	1.3718	1.4076	1.4384	1.4648	1.4879	±.0006
0	.9794	.9992	1.0182	1.0366	1.0543	1.0715	1.0881	1.1042	1.1197	1.1348	1.2032	1.2609	1.3095	1.3504	1.3854	1.4161	1.4440	1.4706	±.0006
0	.937	.958	.978	.997	1.016	1.034	1.051	1.067	1.083	1.099	1.167	1.224	1.272	1.313	1.349	1.380	1.408	1.432	±.002
0	.886	.908	.928	.949	.968	.986	1.004	1.021	1.038	1.054	1.125	1.183	1.233	1.274	1.311	1.342	1.370	1.395	±.002
0	.826	.849	.872	.893	.914	.934	.953	.971	.989	1.006	1.080	1.141	1.192	1.235	1.272	1.305	1.334	1.359	±.003
0	.751	.776	.800	.824	.846	.867	.888	.908	.927	.946	1.028	1.095	1.151	1.197	1.236	1.269	1.298	1.323	±.005
0	.639	.675	.709	.741	.771	.799	.825	.850	.873	.895	.986	1.054	1.108	1.153	1.193	1.229	1.261	1.285	±.005

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Table 5. Density of NaOH Solutions (g/cm^3).

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Temp. (°C)	CONCENTRATION (WEIGHT PERCENT)	

Temp. (°C)	1	3	5	7	9	11	13	15	20	25	30	35	40	45	50	±
0	1.0124	1.0364	1.0597	1.0828	1.1057	1.1285	1.1512	1.1738	1.2299	1.2853	1.3397	1.3925	1.4434	1.4924	1.5399	±.0003
-25	1.00813	1.03004	1.0519	1.0737	1.0956	1.1175	1.1395	1.1614	1.2163	1.2708	1.3244	1.3768	1.4274	1.4757	1.5210	±.0003
50	.99876	1.01984	1.0409	1.0620	1.0832	1.1046	1.1260	1.1476	1.2018	1.2559	1.3089	1.3602	1.4092	1.4563	1.5039	±.0006
70	.9884	1.0093	1.0302	1.0511	1.0721	1.0933	1.1145	1.1357	1.1892	1.2425	1.2952	1.3467	1.3963	1.4435	1.4879	±.0006
100	.9692	.9903	1.0113	1.0323	1.0534	1.0745	1.0957	1.1170	1.1704	1.2236	1.2757	1.3261	1.3744	1.4214	1.4707	±.0006
150	.926	.948	.971	.993	1.015	1.037	1.059	1.081	1.134	1.187	1.238	1.288	1.337	1.386	1.432	±.002
200	.875	.898	.921	.944	.967	.990	1.012	1.035	1.091	1.145	1.198	1.249	1.299	1.348	1.395	±.002
250	.814	.839	.864	.888	.913	.938	.962	.986	1.045	1.102	1.157	1.209	1.260	1.310	1.359	±.003
300	.739	.765	.792	.818	.845	.871	.898	.924	.989	1.052	1.112	1.170	1.224	1.274	1.323	±.005
350	.621	.659	.697	.734	.769	.804	.837	.869	.944	1.011	1.071	1.126	1.180	1.235	1.285	±.005

Table 6. Interpolation equation coefficients for NaOH solutions.

The available density data for temperatures between $0°$ and $100°C$ were converted to apparent molal volume and fit by the method of least squares to a polynomial equation of the form

$$\phi_v = \sum_{j=0}^{n} A_j m^{j/2}, \text{ where m is the molality of the solution.}$$

Density may be calculated by using the formula

$$d = \frac{1000 d_0 + M_2 m d_0}{1000 + \phi_v m d_0}, \text{ where } M_2 = 39.997 \text{ g/mole}$$
and d_0 is the density of water

The interpolation equations are valid only for concentrations less than 26 molal (51 wt%).

Temp. (°C)	n	A_0	A_1	A_2	A_3	A_4	d_0
0	2	-13.313	7.667	-.5232	-------	-------	.999840
25	4	-5.2618	1.982	1.2730	-.28035	.017674	.997047
50	4	-4.8480	3.7608	-.14493	.08709	-.013618	.988038
70	4	-4.4239	2.5852	.71785	-.14439	.007130	.977766
100	4	-7.5513	5.3277	-.60261	.16848	-.020118	.958357

For temperatures between $150°$ and $350°C$, the available data were fit by the method of least squares to a polynomial equation of the form

$$d = \sum_{j=0}^{4} B_j m^j.$$

The interpolation equations are valid only for concentrations less than 26 molal (51 wt%).

Temp. (°C)	B_0	$10 \times B_1$	$-10^2 \times B_2$	$10^4 \times B_3$	$-10^6 \times B_4$
150	.91499	.44439	.17615	.45910	.53917
200	.86315	.46138	.18182	.45662	.50933
250	.80098	.50260	.21281	.56943	.66109
300	.72533	.52969	.19847	.42286	.37630
350	.60082	.79142	.48458	1.7063	2.38441