UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY



# THE VOLUMETRIC PROPERTIES OF VAPOR-SATURATED AQUEOUS $Na_2CO_3$ SOLUTIONS FROM 0°C TO 100°C, VAPOR-SATURATED AQUEOUS $K_2CO_3$ SOLUTIONS FROM 0°C TO 100°C, VAPOR-SATURATED AQUEOUS $KHCO_3$ SOLUTIONS FROM 0°C TO 50°C, AND VAPOR-SATURATED AQUEOUS $NaHCO_3$ SOLUTIONS FROM 18°C TO 60°C BASED ON A REGRESSION OF THE AVAILABLE LITERATURE DATA

by

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Open-file report
77-321

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 the production of electricity. Precise thermodynamic data derived from the volumetric properties of the brines are prerequisite for chemical and reservoir modeling 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, $CaCl_2$, $Na_2SO_4$, $K_2SO_4$, KOH, NaOH, HCl, $FeCl_2$, $FeCl_3$, $H_2SO_4$, $FeSO_4$, $NaHSO_4$, and $KHSO_4$ have been completed (Potter and Brown, 1975, 1976a, 1976b, 1976c; Potter and Clynne, 1976; Brown and Potter, 1977a, 1977b, 1977c).

Prior to this report, the only extensive tabulation of volumetric data for aqueous vapor-saturated sodium carbonate, potassium carbonate, sodium bicarbonate, and potassium bicarbonate was the International Critical Tables (National Research Council, 1928). A compilation of density values is presented therein for vapor-saturated $Na_2CO_3$ solutions of 0 to 14 weight percent concentrations from 0°C to 100°C, for vapor-saturated $K_2CO_3$ solutions of 0 to 50 weight percent concentrations from 0°C to 100°C, for vapor-saturated $NaHCO_3$ solutions of 0 to 8 weight percent concentrations at 18°C, and for vapor-saturated $KHCO_3$ solutions of 0 to 35 weight percent concentrations from 0° to 50°C. There are no compilations available for these solutions at pressures greater than the saturation vapor pressure (Potter, 1976). The purpose of this report is to present an internally consistent set of

of density values for vapor-saturated $Na_2CO_3$ solutions from 0°C to 100°C, for vapor-saturated $K_2CO_3$ solutions from 0°C to 100°C, for vapor-saturated $NaHCO_3$ solutions from 18°C to 60°C, and for vapor-saturated $KHCO_3$ solutions from 0°C to 50°C, based on the currently available experimental data, the references for which are summarized by Potter et al. (1975).

The density data presented in tables 1, 2, 4, 5, 7, 8, and 10 were obtained from a regression of the available P-V-T-X data for $Na_2CO_3$, $K_2CO_3$, $NaHCO_3$, and $KHCO_3$. These data were taken from the International Critical Tables and the 35 references cited by Potter et al. (1975). The regression of the data 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. Data which did not meet Chauvenet's criterion were either not used or were weighted very lightly in the fits.

The experimental densities were fit at constant temperatures as a function of composition for each solute. For $Na_2CO_3$, $KHCO_3$, and $NaHCO_3$, a second-order polynomial equation relating the density, d, and the molality, m, of the solution,

$$d = A + Bm^{\frac{1}{2}} + Cm, \qquad (1)$$

was used for regression purposes. The standard deviation of the resulting equations was found to represent the internal consistency of the data used in the fit quite adequately. Very precise measurements of the density of $K_2CO_3$ solutions are available and these could not be represented adequately by an equation of this form. It was found that by converting

the density data to apparent molal volume, $\phi_v$, and then fitting this to an equation of the form

$$\phi_v = A_o + B_o m^{\frac{1}{2}} + C_o m, \qquad (2)$$

a much more accurate fit could be obtained. The density can then be recalculated from the apparent molal volume by using the relation

$$d = \frac{1000\, d_o + M_2 m d_o}{1000 + \phi_v m d_o}, \qquad (3)$$

where $M_2$ is the molecular weight of the solute and $d_o$ is the density of water.

Tables 3, 6, 9, and 10 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 not included in the density tabulations. The uncertainties quoted in the tables were chosen so that 95% of the experimental data points used in the fit would lie within the range given. It should be noted that the equations in Tables 3, 9, and 10 do not extrapolate through the density of water. This difficulty arises due to a lack of data at concentrations less than 1% and because of inconsistencies in the experimental data sets probably resulting from equilibration with atmospheric $CO_2$.

Due to an inadequate data base, it was not possible to generate a set of density values at pressures greater than the saturation vapor pressure for the solutions discussed in this paper which would accurately represent the behavior of each solution above its saturation surface.

## REFERENCES

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Table 1: Density of $Na_2CO_3$ Solutions ($g/cm^3$).

| Temp. (°C) | Concentration (molality) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | .2 | .4 | .6 | .8 | 1.0 | 1.2 | 1.4 | |
| 0 | 1.0232 | 1.0451 | 1.0656 | 1.0853 | 1.1046 | 1.1236 | 1.1422 | ± .0007 |
| 25 | 1.0190 | 1.0389 | 1.0581 | 1.0770 | 1.0957 | 1.1142 | 1.1326 | ± .0008 |
| 50 | 1.0089 | 1.0287 | 1.0476 | 1.0659 | 1.0840 | 1.1018 | 1.1195 | ± .0006 |
| 70 | .9980 | 1.0175 | 1.0361 | 1.0543 | 1.0722 | 1.0899 | 1.1075 | ± .0006 |
| 100 | .9793 | .9990 | 1.0177 | 1.0358 | 1.0535 | 1.0710 | 1.0883 | ± .0006 |

Table 2: Density of $Na_2CO_3$ Solutions ($g/cm^3$).

| Temp. (°C) | Concentration (weight percent) 1 | 3 | 5 | 7 | 9 | 11 | 13 | |
|---|---|---|---|---|---|---|---|---|
| 0 | 1.0104 | 1.0335 | 1.0551 | 1.0705 | 1.0982 | 1.1204 | 1.1432 | ± .0007 |
| 25 | 1.0079 | 1.0282 | 1.0482 | 1.0686 | 1.0895 | 1.1111 | 1.1335 | ± .0008 |
| 50 | .9976 | 1.0182 | 1.0379 | 1.0577 | 1.0780 | 1.0988 | 1.1203 | ± .0006 |
| 70 | .9870 | 1.0071 | 1.0265 | 1.0462 | 1.0662 | 1.0869 | 1.1083 | ± .0006 |
| 100 | .9670 | .9885 | 1.0081 | 1.0277 | 1.0476 | 1.0080 | 1.0891 | ± .0006 |

Table 3: Interpolation Coefficients for $Na_2CO_3$.

The interpolation equation: $d = A + Bm^{\frac{1}{2}} + Cm$

is valid for concentrations from .1 to 1.5 molal (1 to 14 weight percent)

| Temp. (°C) | A | B | C |
|---|---|---|---|
| 0 | .9927 | .0328 | .0791 |
| 25 | .9949 | .0158 | .0850 |
| 50 | .9832 | .0223 | .0785 |
| 70 | .9734 | .0196 | .0792 |
| 100 | .9530 | .0250 | .0755 |

Table 4: Density of $K_2CO_3$ Solutions ($g/cm^3$).

| Temp. (°C) | Concentration (molality) 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 | 5.0 | 5.5 | 6.0 | 6.5 | 7.0 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 1.0619 | 1.1174 | 1.1683 | 1.2153 | 1.2588 | 1.2992 | 1.3369 | 1.3719 | 1.4047 | 1.4354 | 1.4641 | 1.4912 | 1.5166 | 1.5406 | ± .0002 |
| 25 | 1.0559 | 1.1093 | 1.1587 | 1.2047 | 1.2475 | 1.2874 | 1.3246 | 1.3594 | 1.3920 | 1.4224 | 1.4509 | 1.4776 | 1.5027 | 1.5262 | ± .0005 |
| 50 | 1.0454 | 1.0978 | 1.1464 | 1.1918 | 1.2342 | 1.2738 | 1.3108 | 1.3455 | 1.3779 | 1.4083 | 1.4367 | 1.4633 | 1.4883 | 1.5117 | ± .0005 |
| 70 | 1.0343 | 1.0862 | 1.1347 | 1.1799 | 1.2222 | 1.2619 | 1.2990 | 1.3337 | 1.3662 | 1.3966 | 1.4250 | 1.4516 | 1.4765 | 1.4998 | ± .0005 |
| 100 | 1.0155 | 1.0678 | 1.1165 | 1.1620 | 1.2045 | 1.2442 | 1.2814 | 1.3162 | 1.3486 | 1.3790 | 1.4073 | 1.4338 | 1.4586 | 1.4817 | ± .0005 |

Table 5: Density of $K_2CO_3$ Solutions ($g/cm^3$).

| Temp. (°C) | Concentration (weight percent) 1 | 3 | 5 | 7 | 9 | 11 | 13 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 1.0096 | 1.0287 | 1.0478 | 1.0670 | 1.0864 | 1.1060 | 1.1259 | 1.1461 | 1.1977 | 1.2513 | 1.3070 | 1.3648 | 1.4248 | 1.4869 | 1.5515 | ± .0002 |
| 25 | 1.0062 | 1.0243 | 1.0425 | 1.0608 | 1.0795 | 1.0984 | 1.1176 | 1.1371 | 1.1875 | 1.2401 | 1.2951 | 1.3524 | 1.4119 | 1.4735 | 1.5368 | ± .0005 |
| 50 | 0.9969 | 1.0145 | 1.0323 | 1.0502 | 1.0685 | 1.0870 | 1.1059 | 1.1252 | 1.1748 | 1.2269 | 1.2815 | 1.3384 | 1.3978 | 1.4592 | 1.5222 | ± .0005 |
| 70 | 0.9865 | 1.0038 | 1.0213 | 1.0391 | 1.0572 | 1.0756 | 1.0943 | 1.1135 | 1.1630 | 1.2150 | 1.2696 | 1.3267 | 1.3861 | 1.4475 | 1.5102 | ± .0005 |
| 100 | 0.9672 | 0.9847 | 1.0024 | 1.0203 | 1.0385 | 1.0570 | 1.0759 | 1.0952 | 1.1450 | 1.1972 | 1.2519 | 1.3091 | 1.3685 | 1.4297 | 1.4920 | ± .0005 |

Table 6: Interpolation Coefficients for $K_2CO_3$.

The available density data was converted to apparent molar volume $\phi_v$ and fit to an equation of the form

$$\phi_v = A_o + B_o m^{\frac{1}{2}} + C_o m ,$$

where m is the molality of the solution. Density, d, may be calculated using the formula

$$d = \frac{1000\, d_o + M_2 m d_o}{1000 + \phi_v m d_o} ,$$

where $d_o$ is the density of water and $M_2 = 138.213$ g-mole$^{-1}$ is the molecular weight of $K_2CO_3$. The equations are valid for concentrations of 0 to 7 molal (0 to 50 weight percent).

| Temp. (°C) | $A_o$ | $B_o$ | $C_o$ | $d_o$ (g/cm$^3$) |
|---|---|---|---|---|
| 0 | -.9931 | 22.0203 | -2.5301 | .999840 |
| 25 | 8.4831 | 16.0445 | -1.4357 | .997047 |
| 50 | 11.800 | 13.983 | -1.065 | .988038 |
| 70 | 13.434 | 12.360 | -0.6904 | .977766 |
| 100 | 9.0915 | 14.306 | -0.9015 | .958357 |

Table 7: Density of $KHCO_3$ ($g/cm^3$).

| Temp. (°C) | Concentration (weight percent) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 3 | 5 | 7 | 9 | 11 | 13 | 15 | 17 | 19 | 21 | 23 | 25 | 30 | 35 |
| 0 | 1.0067 | 1.0199 | 1.0346 | -- | -- | -- | -- | 1.1231 | | | | | | | |
| 10 | 1.0065 | 1.0197 | 1.0345 | -- | -- | -- | -- | -- | 1.1442 | | | | | | |
| 15 | 1.0056 | 1.0193 | 1.0327 | 1.0463 | 1.0603 | 1.0747 | -- | -- | -- | -- | | | | | |
| 20 | 1.0051 | 1.0182 | 1.0330 | -- | -- | -- | -- | -- | -- | 1.1664 | | | | | |
| 25 | 1.0040 | 1.0170 | 1.0318 | -- | -- | -- | -- | -- | -- | -- | 1.1879 | | | | |
| 30 | 1.0026 | 1.0157 | 1.0306 | -- | -- | -- | -- | -- | -- | -- | 1.1877 | | | | |
| 40 | 0.9992 | 1.0124 | 1.0272 | -- | -- | -- | -- | -- | -- | -- | -- | 1.2062 | | | |
| 50 | 0.9947 | 1.0089 | 1.0213 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | 1.2338 |

**The estimated error is ± .0005 $g/cm^3$ for all densities given.**

Table 8: Density of $KHCO_3$ ($g/cm^3$).

| Temp. (°C) | Concentration (molality) | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | .25 | .50 | .75 | 1.00 | 1.25 | 1.50 | 1.75 | 2.00 | 2.25 | 2.50 | 2.75 | 3.00 | 3.50 | 4.00 | 4.50 | 5.00 | 5.50 |
| 0 | 1.0160 | 1.0329 | -- | -- | -- | -- | 1.1222 | | | | | | | | | | |
| 10 | 1.0158 | 1.0327 | -- | -- | -- | -- | -- | 1.1409 | | | | | | | | | |
| 15 | 1.0156 | 1.0311 | 1.0462 | 1.0610 | 1.0756 | -- | -- | -- | -- | | | | | | | | |
| 20 | 1.0143 | 1.0312 | -- | -- | -- | -- | -- | -- | -- | 1.1782 | | | | | | | |
| 25 | 1.0132 | 1.0300 | -- | -- | -- | -- | -- | -- | -- | 1.1763 | | | | | | | |
| 30 | 1.0119 | 1.0288 | -- | -- | -- | -- | -- | -- | -- | -- | 1.1948 | | | | | | |
| 40 | 1.0085 | 1.0254 | -- | -- | -- | -- | -- | -- | -- | -- | -- | 1.2075 | | | | | |
| 50 | 1.0052 | 1.0199 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | 1.2387 |

The estimated error is ± .0005 $g/cm^3$ for all densities given.

Table 9: Interpolation Coefficients for $KHCO_3$.

The interpolation coefficients given below are for the equation

$$d = A + Bm^{\frac{1}{2}} + Cm ,$$

where m is the molality of the solution. The equations are valid only for the ranges of concentration given.

| | 0°C | 10 | 15 | 20 | 25 | 30 | 40 | 50 |
|---|---|---|---|---|---|---|---|---|
| A | 1.0028 | 1.0028 | 0.9969 | 1.0019 | 1.0006 | 0.9992 | 0.9953 | 0.9817 |
| B | -0.0123 | -0.0131 | 0.0106 | -0.0153 | -0.0146 | -0.0147 | -0.0126 | 0.0301 |
| C | 0.0775 | 0.0783 | 0.0535 | 0.0802 | 0.0795 | 0.0800 | 0.0780 | 0.0339 |
| range of validity | 1-15 wt% | 1-17 wt% | 1-11 wt% | 1-19 wt% | 1-21 wt% | 1-21 wt% | 1-23 wt% | 1-35 wt% |
| | ± .005 | ± .005 | ± .005 | ± .005 | ± .005 | ± .005 | ± .005 | ± .005 |

Table 10: Density of $NaHCO_3$ Solutions at 18°C.

| Concentration | | Density |
|---|---|---|
| molality | weight percent | $g/cm^3$ |
| .12 | 1.00 | 1.0058 |
| .25 | 2.06 | 1.0137 |
| .37 | 3.00 | 1.0206 |
| .50 | 4.03 | 1.0282 |
| .63 | 5.00 | 1.0354 |
| .75 | 5.93 | 1.0423 |
| .90 | 7.00 | 1.0505 |
| 1.00 | 7.75 | 1.0562 |
| 1.04 | 8 | 1.0582 |
| 1.09 | 8.4 (sat) | 1.061 |
| | | $\pm$ .0002 |

The interpolation equation $d = .9969 + .0078\ m^{1/2} + .0515\ m$ is valid for concentrations from 1.0 to 8.4 weight percent (saturation) at 18°C. The density of saturated solutions for temperatures from 20°C to 60°C can be found using

$$d = 1.049 + (6.6 \times 10^{-4})t \quad \pm .001\ g/cm^3\ ,$$

where t is temperature in degrees Celsius.