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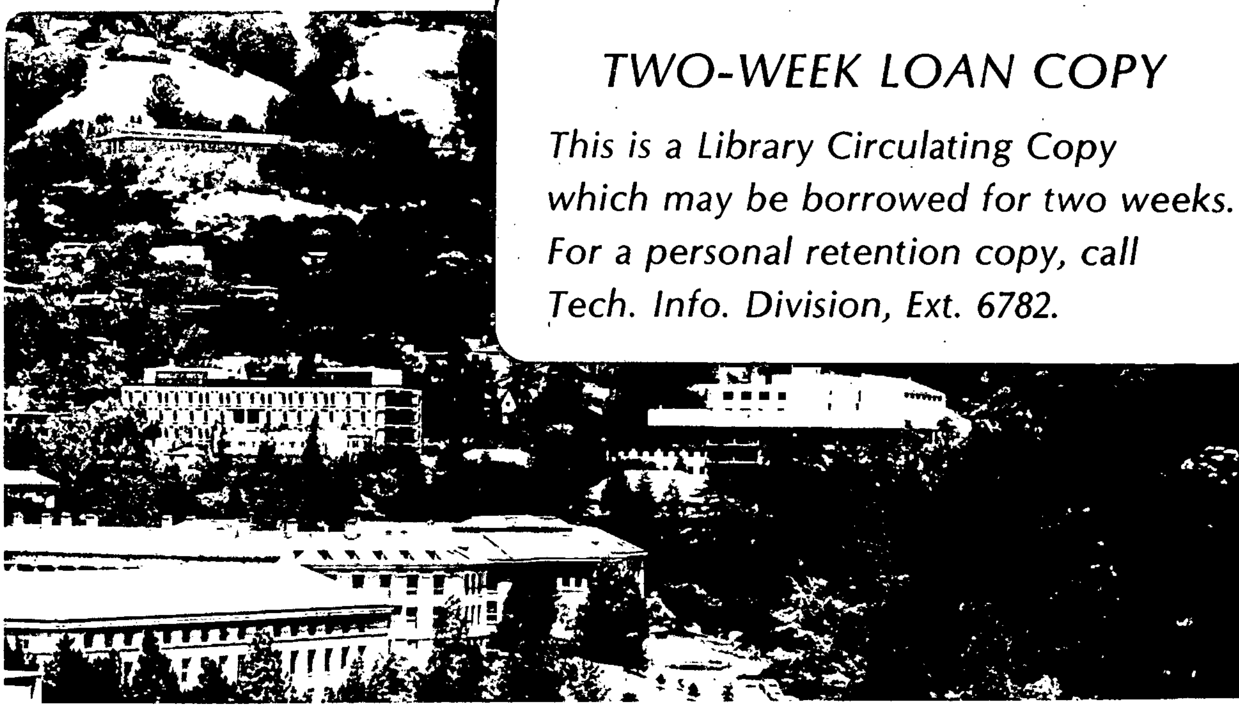

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Thermal Conductivity of Aqueous Sodium Chloride Solutions from 20°C to 330°C

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Selected thermal conductivity data reported in the literature for aqueous sodium chloride solutions are tabulated for geothermal energy applications. Experimental values were converted where necessary to a set of consistent units of °C, molal concentration and watts/m - °C. A selected empirical equation is given to reproduce the data over the temperature range 20°C to 330°C, concentrations between 0 and 5 molal, and at saturation pressures. A table of smoothed values is generated using the correlation which reproduces the experimental data to ±2% up to 80°C. Between 100°C and 150°C, the percent deviation is +17% to +31% for the one set of available experimental values. Recommendations for additional data needs are given. New data are included in this revision.

An important facet in the development and utilization of geothermal energy is the thermodynamic and transport data for the hot brines which transport heat, and the vapors which drive turbines to produce electricity. While geothermal brines contain a large number of dissolved electrolytes and gases, the main constituent is sodium chloride. Consequently, modeling and other studies which require basic data on geothermal brines are generally based on those of aqueous NaCl solutions (1, 2). While data on many basic properties are needed, this report covers a survey of the available data on the thermal conductivity of aqueous NaCl solutions for regions of geothermal interest: temperatures to 350°C, pressures to 500 bars (50 MPa), and concentrations up to saturation.

The current published literature on the thermal conductivity of sodium chloride solutions to high temperatures is not extensive; this is especially true for work at temperatures exceeding 80°C. Only one series of measurements are available to 150°C: these are the data published by Korosi and Fabuss for application to seawater desalination (3, 4). By far, the most extensive data are contained in graphical form in the publication by Yusufova, Pepinov, Nikolaev and Gušeinov with over 50 data points between 100°C and 330°C (5). However, accurate values cannot be read from the graphs.

Unless otherwise noted, the data were compiled from the original publications. Numerical values were converted where necessary to units of °C, molal concentration, and watts / m - °C. The density data needed to convert molar to molal concentrations were obtained from the paper by Rowe and Chou (6). Data on the thermal conductivity of water and the corresponding correlation equation are contained in publications of the International Conference on the Properties of Steam (7, 8).

Additional information on the theory and instrumentation is obtained from Thermal Conductivity (9); theory and correlations from the publications by Kestin and Whitelaw (8), Riedel (10), Korosi and Fabuss (3, 4) and Yusufova, Pepinov, Nikolaev and Guseinov (5). Tabulated data for sodium chloride solutions are given in Table 1. Of special interest are the survey by Jamieson, Irving and Tudhope (11), and the correlation developed for sea water by Jamieson and Tudhope (12).

Scope of Compilation

The time span covered is mainly from 1929 to December 1979; earlier data are found in the International Critical Tables (13). Besides data on the thermal conductivity of aqueous sodium chloride solutions, selected portions of the available literature are included on theory, instrumentation, data estimation methods, other salts (e.g., potassium chloride), and sea water.

Analytical Expressions and Correlations

This section covers selected analytical expressions and empirical correlations which have been used to describe the variation in thermal conductivity for NaCl solutions as a function of concentration and temperature.

Based on theoretical considerations, Predvoditelev (21) and Vargaftik and Os'minin (14) developed the following equation for predicting the thermal conductivity of aqueous solutions:

$$\frac{\lambda}{\lambda_w} = \frac{C_p}{C_{pw}} \left(\frac{\rho}{\rho_w}\right)^{4/3} \left(\frac{M_w}{M}\right)^{1/3} \qquad (1)$$

Vargaftik and Os'minin (14) measured the thermal conductivity of various aqueous solutions including NaCl solutions at 30^{o}C and found that the deviation between the measured and the predicted values by Equation 1 were no more than 5%. The only exception was nitric acid solutions, for which the deviation increased as the acid concentration increased to a maximum deviation of 12%.

Riedel developed an equation which has been used to describe the variation in thermal conductivity with temperature and concentration of salt solutions such as NaCl (10,15):

$$\lambda = \lambda_w + \sum_i a_i \; C_i \qquad (2)$$

a_i = experimentally determined coefficient characteristic for each ion, (-0.0047 for Cl^-, referred to Na^+ as 0)

C_i = concentration of each electrolyte

Korosi and Fabuss (3,4) measured the thermal conductivity for 0.7069m NaCl and 3.5345m NaCl, over the temperature range 25°C-150°C. The authors obtained 12 data points and developed the following polynomial fits for these two concentrations:

$$\begin{aligned} &0.7069\text{m NaCl:} \quad \lambda = 0.540 + 0.001567T - 0.00001397T^2 \\ &3.5345\text{m NaCl:} \quad \lambda = 0.553 + 0.000821T - 0.00000986T^2 \end{aligned} \tag{3}$$

The six values for each concentration were reproduced to better than 1% by Equation (3).

Yusufova, et al. measured the thermal conductivity of aqueous sodium chloride solutions for temperatures ranging from 20°C to 330°C and concentrations of 5, 10, 15, 20 and 25 weight percent NaCl. They developed the following correlation equation which reproduces their experimental data for over 50 values with a reported deviation of 2%:

$$\begin{aligned} \frac{\lambda}{\lambda_W} = 1.0 &- (2.3434 \times 10^{-3} - 7.924 \times 10^{-6}\, T + 3.924 \times 10^{-8}\, T^2)\, S + \\ &(1.06 \times 10^{-5} - 2 \times 10^{-8}\, T + 1.2 \times 10^{-10}\, T^2)\, S^2 \end{aligned} \tag{4}$$

where

$$S = \frac{5844.3 \times m}{1000 + 58.443 \times m}$$

However, numerical data are not available for these measurements, and accurate values cannot be obtained from the figures in the publication. For this reason their data are not included in Table 1.

Unterberg developed a family of curves which depict changes in the thermal conductivity of NaCl solution with temperatures to 149°C, and for zero to saturation concentrations. Unterberg assumed that the variation of thermal conductivity with temperature followed the same trend for different NaCl concentrations as that for pure water (16).

In related work, Jamieson and Tudhope fit experimental data on the thermal conductivity of sea water solutions to the following equation:

$$\ln \lambda = \ln (\lambda_w + X) + (2.3 - \frac{G}{T})(1 - \frac{T}{T_c + Y})^{0.333} \qquad (5)$$

where T_c = 647^{o}K (critical temperature of distilled water)

X = salinity x 0.0002, Y = salinity x 0.003 and

G = 343.5 + (salinity x 0.37)

Equation 5 fits the experimental data to ±3% for salinities between 0 and 160 g/kg, and temperatures from 0^{o}C to 80^{o}C. For distilled water, the data are fit with an error not greater than 1.3% up to 400^{o}C (12).

In summary, correlations are available which reproduce data on the thermal conductivity of NaCl solutions at vapor saturation pressures and in the temperature and concentration regions of interest for geothermal energy.

Methods for Measuring Thermal Conductivity

The methods commonly used to measure the thermal conductivity of aqueous solutions include the following: coaxial cylinders, flat plate, and continuous line source. The first two are steady state methods; the third is a transient method.

Chernen'kaya and Vernigora measured the thermal conductivity of NaCl and other solutions at 25^{o}C and 50^{o}C using a cell comprised of two coaxial thin-walled glass cylinders (17). The NaCl solution was placed between the cylinders, and the inner cell was thermostated to 25^{o}C or 50^{o}C for 30 minutes. The difference in temperature across the NaCl solution was measured by a differential thermocouple. The instrument was calibrated with doubly distilled gas-free water, methyl alcohol and benzene. Tufeu, Le Neindre and Johannin also used the coaxial cylinder method in their measurements (18). The measured values are believed accurate to within about ±5% (12). This method was also used by Riedel (10).

Yusufova, et al. used a flat plate method for measuring the thermal conductivity of NaCl from 25°C to 330°C (5). The solution was placed between an upper and a lower circular metal plate; the upper plate was maintained at a high temperature to provide downward heat flow to prevent natural convection. A guard heater was located on the periphery both to assure linear heat flow, and to minimize convection. The main difficulties with this method center on maintaining linear heat flow and eliminating convection around the edges of the heated plates. Kapustinski and Ruzavin used a cell consisting of three silvered copper plates, 1 cm apart and forming two chambers. One chamber was used to hold a standard liquid, and the other the NaCl solution. The standard was double distilled water. The temperature was maintained to 0.001°C, and the error of measurements was stated to be ±0.1% (20).

The non-steady state method such as the continuous line source method has been widely used. In this case, heat is generated at a constant rate in a long, thin wire which is inserted in a large volume of test liquid. The system is initially at a constant temperature; heat is then applied, and the thermal conductivity of NaCl is determined from the measurements of temperature vs. time at a fixed distance from the wire. Vargaftik and Os'minin (14), Chiquillo (19) and Korosi and Fabuss(3,4) used this method in their thermal conductivity measurements. Jamieson and Tudhope used the relative hot-wire method to measure values for sea water solutions in the temperature range 0°C to 125°C (12).

Evaluation and Correlation

The data were converted where necessary to the ^{12}C scale of atomic weights, to units of g/cm^3 for density, to watts/m-°C for thermal conductivity, to molal concentrations, and from relative values of thermal conductivity to absolute values for NaCl solutions. The required data and interpolating equation for the thermal conductivity of water were taken from the report on the results of the Sixth International Conference on the Properties of Steam (7,8).

The correlation given by Yusufova is the only one available which represents a large number of data points in the temperature and pressure range of geothermal interest. As seen, Equation (5) is the ratio of the thermal conductivity of NaCl solutions to that of pure water. Yusufova used the following equation for liquid water which was contained in the publications on the Sixth International Conference on the Properties of Steam (7,8).

$$\lambda_W = -0.92247 + 2.8395 \left(\frac{T + 273.15}{273.15}\right) - 1.8007 \left(\frac{T + 273.15}{273.15}\right)^2 + 0.52577 \left(\frac{T + 273.15}{273.15}\right)^3 - 0.07344 \left(\frac{T + 273.15}{273.15}\right)^4 \qquad (6)$$

Equation (6) is valid for temperatures ranging from $0^{o}C$ to $350^{o}C$ at saturation pressures.

Equations (4) and (6) were selected in this work to reproduce and interpolate data on the thermal conductivity of NaCl solutions. Figure 1 shows the variation in thermal conductivity for concentrations from 0 to 5m NaCl and temperatures between $50^{o}C$ and $300^{o}C$. As shown, the thermal conductivity decreases almost linearly at each temperature as the concentration increases. Figure 2 is a plot of thermal conductivity versus temperature with concentration as a parameter. The thermal conductivity increases with increasing temperatures up to a broad maximum near $140^{o}C$, then decreases with concentration, by a maximum of 7% for 5m NaCl as compared with pure water. Table 2 consists of smoothed values for the thermal conductivity of aqueous NaCl solutions from $20^{o}C$ to $330^{o}C$ over the concentration range 0 to 5 molal. Table 3 compares the available experimental data with that calculated from Equations (4) and (6).

Summary and Conclusions

The correlation in Equation (4) generally reproduces the experimental data to better than ±2% between $20^{o}C$ and $80^{o}C$; an exception is the data of Korosi and Fabuss where the deviation ranges from +5.3 to +13.8%. See Table 3. Between $100^{o}C$ and $150^{o}C$, the deviation between the calculated values and the data of Korosi and Fabuss increases to +31.6% at $150^{o}C$. However, we assume their values to be incorrect partly because they are consistently higher than the other values at temperatures below $80^{o}C$, and partly because Korosi and Fabuss felt their measurements should be considered tentative (3,4,12). In addition, the values obtained for sea water concentrations to $150^{o}C$ are consistently lower than those of Jamieson and Tudhope(12).

Recommendations

After surveying the current experimental values in light of the data requirements, some specific recommendations are appropriate. While data to 80^{0}C are satisfactory in some respects, there are inadequacies for temperatures to 350^{0}C, and for pressures to 50MPa. Future work should include the following:

1. Development of a theoretical equation to predict the thermal conductivity of NaCl solutions to high temperatures, concentrations and pressures. The equation would permit estimations of values where data do not exist. Currently, the best available approach is that of Rideal, but only for low temperatures and concentrations (15).
2. Additional experimental data are needed above 80^{0}C to augment those of Korosi and Yusufova, and to assist in reconciling the difference in their reported values. Data are also needed for mixtures of sodium chloride solutions with potassium chloride and calcium chloride (24). Thereby, the effects of these salts would be determined so that geothermal brines could be more closely modelled. Data on KCl and $CaCl_2$ solutions are reported to be available (22). Correlations for the thermal conductivity of organic liquids was recently published by Jamieson (23).
3. Investigation of the effect of pressure to 50 MPa. All the current data were obtained at saturation vapor pressures.
4. Laboratory measurements of the thermal conductivity of geothermal brines as a function of concentration, temperature and pressure. The data will provide site-specific information on the variation in thermal conductivity, and to test the applicability of NaCl solutions for modelling.

Glossary

λ : thermal conductivity of aqueous solution, watts/m-^{o}C

λ_w : thermal conductivity of water, watts/m-^{o}C

C_p : heat capacity of aqueous solution, cal/mole-^{o}C

C_{pw} : heat capacity of water, cal/mole-^{o}C

ρ : density of aqueous solution, g/cm^3

ρ_w : density of water, g/cm^3

M : molecular weight of NaCl

M_w : molecular weight of water

m : molality

T : degrees celsius, ^{o}C

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Table 1. Experimental data for thermal conductivity of aqueous NaCl solutions.

Temperature °C	Concentration molal	Thermal Conductivity watts/m-°C	Reference
20	0.901	0.594	Riedel (10)
20	1.901	0.589	Riedel (10)
20	2.700	0.590	Tufeu, et al. (18)
20	3.020	0.583	Riedel (10)
20	4.278	0.578	Riedel (10)
20	4.180	0.583	Tufeu, et al. (18)
20	5.704	0.573	Riedel (10)
20	5.770	0.574	Tufeu, et al. (18)
25	0.707	0.574	Korosi and Fabuss (3)
25	0.741	0.605	Kapustinski and Ruzavin (20)
25	0.872	0.606	Kapustinski and Ruzavin (20)
25	0.901	0.605	Kapustinski and Ruzavin (20)
25	1.573	0.600	Kapustinski and Ruzavin (20)
25	1.802	0.600	Kapustinski and Ruzavin (20)
25	1.849	0.600	Kapustinski and Ruzavin (20)
25	1.944	0.599	Chernen'kaya and Vernigora (17)
25	2.534	0.595	Kapustinski and Ruzavin (20)
25	2.716	0.595	Kapustinski and Ruzavin (20)
25	2.878	0.596	Kapustinski and Ruzavin (20)
25	3.535	0.567	Korosi and Fabuss (3)
25	3.655	0.589	Kapustinski and Ruzavin (20)
25	3.781	0.591	Kapustinski and Ruzavin (20)
25	4.494	0.583	Chernen'kaya and Vernigora (17)
25	4.521	0.587	Kapustinski and Ruzavin (20)
25	4.883	0.587	Kapustinski and Ruzavin (20)
25	5.523	0.582	Kapustinski and Ruzavin (20)
20-40	1.061	0.608	Chiquillo (19)
30	1.901	0.603	Vargaftik and Os'minin (14)
20-40	1.936	0.604	Chiquillo (19)
20-40	2.857	0.592	Chiquillo (19)
20-40	3.434	0.581	Chiquillo (19)
30	4.278	0.589	Vargaftik and Os'minin (14)
40	2.730	0.615	Tufeu, et al. (18)
40	4.220	0.605	Tufeu, et al. (18)
40	5.820	0.594	Tufeu, et al. (18)
50	0.707	0.577	Korosi and Fabuss (3)
50	1.944	0.635	Chernen'kaya and Vernigora (17)
50	3.535	0.571	Korosi and Fabuss (3)
50	4.494	0.617	Chernen'kaya and Vernigora (17)
60	2.760	0.634	Tufeu, et al. (18)
60	4.270	0.623	Tufeu, et al. (18)
60	5.890	0.611	Tufeu, et al. (18)
75	0.707	0.581	Korosi and Fabuss (3)
75	3.535	0.557	Korosi and Fabuss (3)
80	2.790	0.647	Tufeu, et al. (18)
80	4.320	0.635	Tufeu, et al. (18)
80	5.960	0.622	Tufeu, et al. (18)
100	0.707	0.560	Korosi and Fabuss (3)
100	3.535	0.539	Korosi and Fabuss (3)
125	0.707	0.518	Korosi and Fabuss (3)
125	3.535	0.500	Korosi and Fabuss (3)
150	0.707	0.460	Korosi and Fabuss (3)
150	3.535	0.455	Korosi and Fabuss (3) (3)

Table 2 Recommended values for the thermal conductivity of aqueous NaCl solutions, calculated from Equation (4) and (5), watts/m-°C (λ).

Temperature, Deg. Celsius (°C) \ Concentration, Molality (m)	0	1	2	3	4	5
20	0.603	0.596	0.590	0.585	0.580	0.577
30	0.618	0.611	0.605	0.600	0.595	0.592
40	0.632	0.624	0.618	0.613	0.609	0.605
50	0.643	0.636	0.630	0.625	0.621	0.617
60	0.653	0.646	0.640	0.635	0.631	0.627
70	0.662	0.655	0.649	0.644	0.640	0.636
80	0.670	0.663	0.657	0.652	0.647	0.643
90	0.676	0.669	0.663	0.658	0.653	0.649
100	0.681	0.674	0.668	0.662	0.658	0.654
110	0.684	0.677	0.671	0.666	0.661	0.658
120	0.687	0.679	0.673	0.668	0.664	0.660
130	0.688	0.680	0.674	0.669	0.664	0.661
140	0.688	0.680	0.674	0.669	0.664	0.660
150	0.687	0.679	0.673	0.667	0.663	0.659
160	0.684	0.677	0.670	0.665	0.660	0.656
170	0.681	0.673	0.667	0.661	0.656	0.652
180	0.677	0.669	0.662	0.656	0.651	0.647
190	0.671	0.663	0.656	0.650	0.645	0.641
200	0.665	0.656	0.649	0.643	0.638	0.633
210	0.657	0.648	0.641	0.635	0.630	0.625
220	0.648	0.640	0.632	0.626	0.620	0.616
230	0.639	0.630	0.622	0.616	0.610	0.605
240	0.628	0.619	0.611	0.604	0.599	0.594
250	0.616	0.607	0.599	0.592	0.586	0.581
260	0.603	0.594	0.586	0.579	0.573	0.567
270	0.589	0.580	0.571	0.564	0.558	0.553
280	0.574	0.565	0.556	0.549	0.543	0.537
290	0.558	0.548	0.540	0.532	0.526	0.520
300	0.541	0.531	0.522	0.515	0.508	0.503
310	0.523	0.512	0.504	0.496	0.489	0.484
320	0.503	0.493	0.484	0.476	0.470	0.464
330	0.482	0.472	0.463	0.455	0.449	0.443

Table 3. Comparison of experimental data with those calculated from Equation (4) and (6).

Temperature, Deg. Celsius (°C)	Concentration, Molality (m)	Thermal Conductivity Calculated From Equation (4) and (5), watts/m-°C (λ)	Reference	Measured Thermal Conductivity watts/m-°C (λ_m)	% Deviation $\frac{\lambda-\lambda_m}{\lambda} \times 100$
30	1.901	0.606	Vargaftik and Os'minin (14)	0.603	0.5
30	4.278	0.594	Vargaftik and Os'minin (14)	0.589	0.8
25	1.944	0.598	Chernen'kaya and Vernigora (17)	0.599	-0.2
25	4.494	0.586	Chernen'kaya and Vernigora (17)	0.583	0.5
50	1.944	0.631	Chernen'kaya and Vernigora (17)	0.635	-0.6
50	4.494	0.619	Chernen'kaya and Vernigora (17)	0.617	0.3
30	1.061	0.611	Chiquillo (19)	0.608	0.5
30	1.944	0.605	Chiquillo (19)	0.604	0.2
30	2.857	0.601	Chiquillo (19)	0.592	1.5
30	3.434	0.598	Chiquillo (19)	0.581	2.8
20	0.901	0.597	Riedel (10)	0.594	0.5
20	1.901	0.591	Riedel (10)	0.589	0.3
20	3.020	0.585	Riedel (10)	0.583	0.3
20	4.278	0.579	Riedel (10)	0.578	0.2
20	5.704	0.574	Riedel (10)	0.573	0.2
25	0.741	0.606	Kapustinski and Ruzavin (20)	0.605	0.2
25	0.872	0.605	Kapustinski and Ruzavin (20)	0.606	-0.2
25	0.901	0.605	Kapustinski and Ruzavin (20)	0.605	0.0
25	1.573	0.600	Kapustinski and Ruzavin (20)	0.600	0.0
25	1.802	0.599	Kapustinski and Ruzavin (20)	0.600	-0.2
25	1.849	0.599	Kapustinski and Ruzavin (20)	0.600	-0.2
25	2.534	0.595	Kapustinski and Ruzavin (20)	0.595	0.0
25	2.716	0.594	Kapustinski and Ruzavin (20)	0.595	-0.2
25	2.878	0.593	Kapustinski and Ruzavin (20)	0.596	-0.5
25	3.655	0.590	Kapustinski and Ruzavin (20)	0.589	0.2
25	3.781	0.589	Kapustinski and Ruzavin (20)	0.591	-0.3
25	4.521	0.586	Kapustinski and Ruzavin (20)	0.587	-0.2
25	4.883	0.585	Kapustinski and Ruzavin (20)	0.587	-0.3
25	5.523	0.582	Kapustinski and Ruzavin	0.582	0.0
20	2.700	0.590	Tufeu, et al. (18)	0.586	0.7
20	4.180	0.583	Tufeu, et al. (18)	0.580	0.5
20	5.770	0.574	Tufeu, et al. (18)	0.574	0.0
40	2.730	0.615	Tufeu, et al. (18)	0.615	0.0
40	4.220	0.605	Tufeu, et al. (18)	0.608	-0.5
40	5.820	0.594	Tufeu, et al. (18)	0.602	-1.3
60	2.760	0.634	Tufeu, et al. (18)	0.637	-0.5
60	4.270	0.623	Tufeu, et al. (18)	0.630	-1.1
60	5.890	0.611	Tufeu, et al. (18)	0.624	-2.1
80	2.790	0.647	Tufeu, et al. (18)	0.653	-0.9
80	4.320	0.635	Tufeu, et al. (18)	0.646	-1.7
80	5.960	0.622	Tufeu, et al. (18)	0.640	-2.9

Table 3. Comparison of experimental data with those calculated from Equation (4) and (6) (continued).

Temperature, Deg. Celsius (°C)	Concentration, Molality (m)	Thermal Conductivity Calculated From Equation (4) and (5), watts/m-°C (λ)	Reference	Measured Thermal Conductivity watts/m-°C (λ_m)	% Deviation $\frac{\lambda-\lambda_m}{\lambda} \times 100$
25	0.707	0.606	Korosi and Fabuss (3)	0.574	5.3
25	3.535	0.590	Korosi and Fabuss (3)	0.567	3.9
50	0.707	0.638	Korosi and Fabuss (3)	0.577	9.6
50	3.535	0.623	Korosi and Fabuss (3)	0.571	8.3
75	0.707	0.661	Korosi and Fabuss (3)	0.581	12.1
75	3.535	0.646	Korosi and Fabuss (3)	0.557	13.8
100	0.707	0.676	Korosi and Fabuss (3)	0.560	17.2
100	3.535	0.660	Korosi and Fabuss (3)	0.539	18.3
125	0.707	0.682	Korosi and Fabuss (3)	0.518	24.0
125	3.535	0.666	Korosi and Fabuss (3)	0.500	24.9
150	0.707	0.681	Korosi and Fabuss (3)	0.460	32.5
150	3.535	0.665	Korosi and Fabuss (3)	0.455	31.6

Captions

Figure 1. Thermal conductivity of aqueous NaCl solutions as a function of NaCl concentration at temperatures indicated.

Figure 2. Thermal conductivity of aqueous NaCl solutions as a function of temperature at molalities shown.

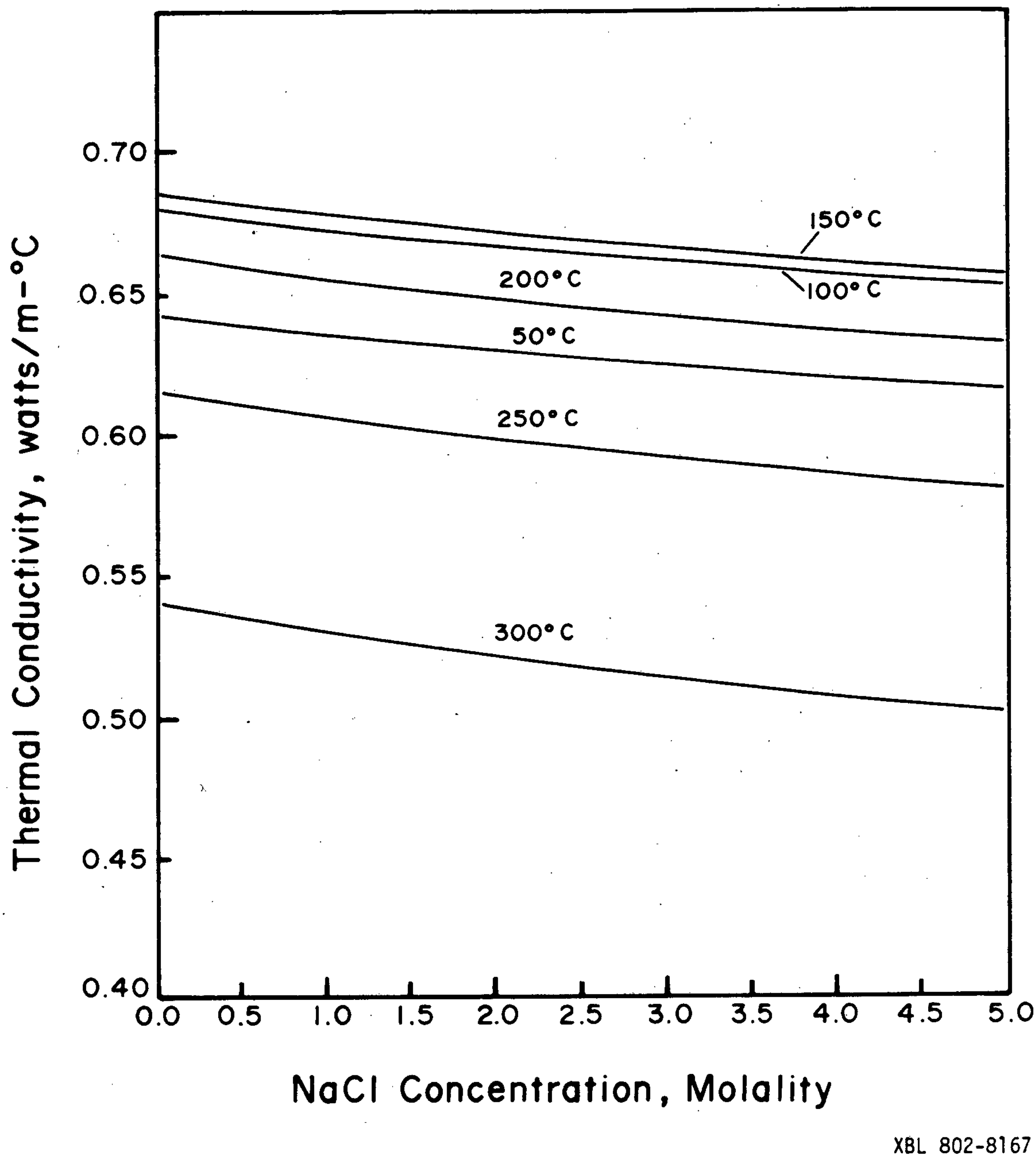
Thermal Conductivity, watts/m-°C
0.70
0.65
0.60
0.55
0.50
0.45
0.40
150°C
100°C
200°C
50°C
250°C
300°C
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
NaCl Concentration, Molality
XBL 802-8167

Fig. 1

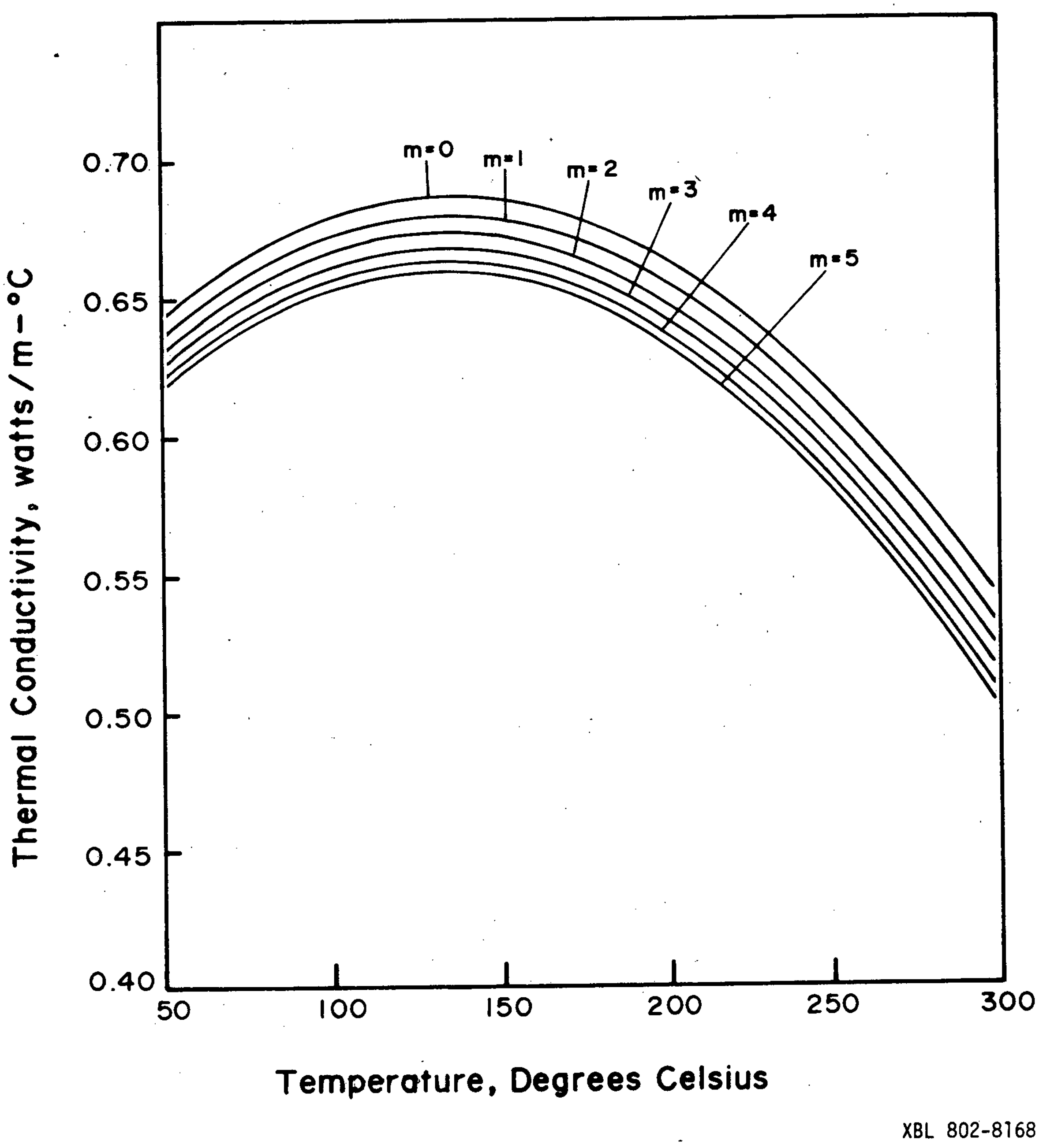
m=0
m=1
m=2
m=3
m=4
m=5
0.70
0.65
0.60
0.55
0.50
0.45
0.40
50
100
150
200
250
300
Thermal Conductivity, watts/m - °C
Temperature, Degrees Celsius
XBL 802-8168

Fig. 2

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