Method for Predicting the Properties of Supersaturated Solutions of the Alkali Chlorides

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A guided extrapolation procedure based on osmotic coefficient data is described for estimating the solution partial pressure, the mean molal activity coefficient, and the activity of the solute for supersaturated aqueous solutions of the alkali chlorides. Data are given for LiCl, NaCl, KCl, RbCl, and CsCl at 25° C. The procedure should be useful for predicting the properties of supersaturated solutions of other compounds.

DURING the course of other work a need arose for values of some of the properties of supersaturated alkali chloride solutions. Unfortunately, the literature contains only fragmentary data on the vapor pressure of supersaturated solutions of potassium chloride. Hence, it became necessary to estimate the required property values. The method employed and the results are given herein.

Initially, the authors attempted to extrapolate the semi-theoretical relationship of Harned and Owen (*1*), this being an extension of the Debye-Hückel "limiting law" for the activity coefficients of electrolytes. However, the equation, involving three empirical parameters, did not yield acceptable results for the osmotic coefficient of LiCl solutions at concentrations less than 2.0 or larger than 10.0 molal. The region of acceptable agreement with experimental data in the case of the other alkali chlorides was still smaller. An empirical approach was substituted, therefore.

At 25° C., lithium chloride is soluble to a concentration of 20.0 molal and cesium chloride to 11.0 molal. Intermediate members of the series are much less soluble: sodium chloride to 6.1, potassium chloride to 4.8, and rubidium chloride to 5.0 molal. Using experimental osmotic coefficient data at 25° C. as reported by Robinson and Stokes (*2*), the ratio of coefficients for each of the alkali chlorides in aqueous solutions relative to that of lithium chloride was plotted as a function of solution concentration. As indicated in Figure 1, this resulted in a family of curves that could be extrapolated following the shape of the curve for cesium chloride to concentrations of 16 molal and beyond. This extrapolation, although not linear, may be made

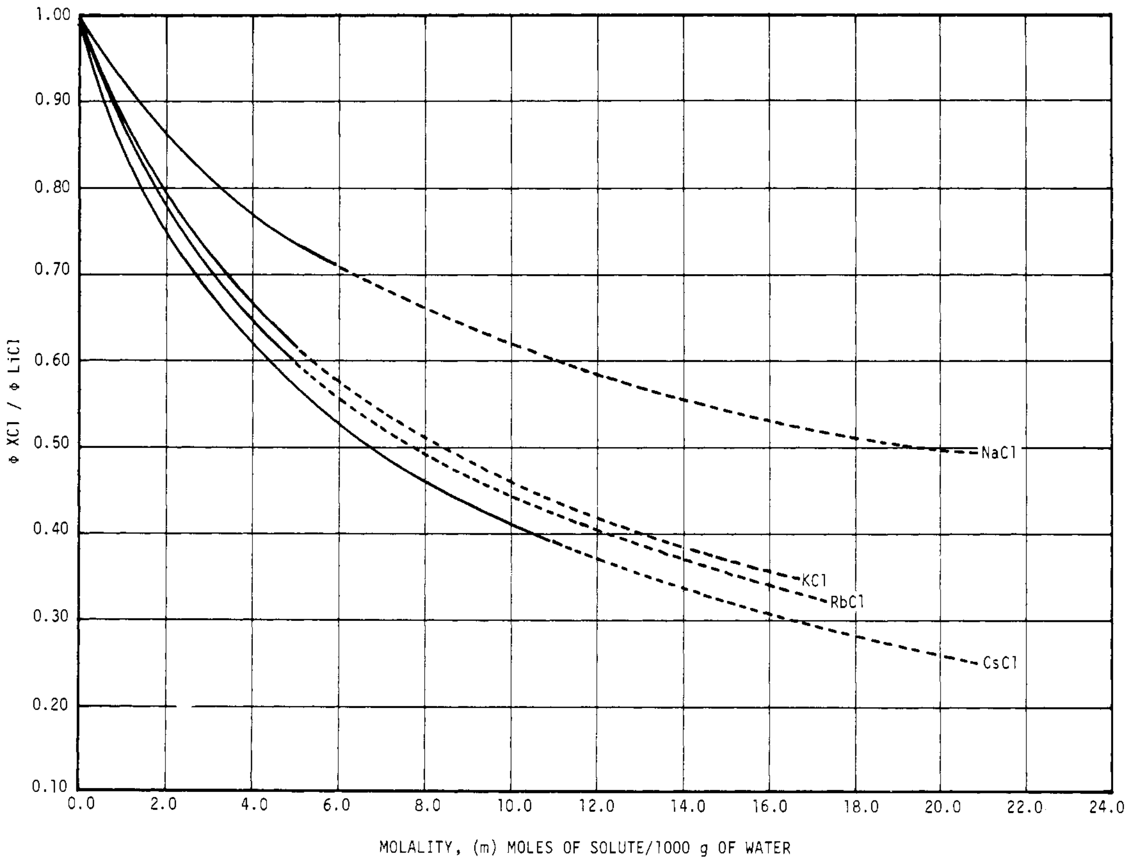

Figure 1. Osmotic coefficient ratios of alkali chlorides relative to lithium chloride in aqueous solutions at 25° C.

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Table I. Aqueous Solution Properties at 25° C. as Predicted

Lithium Chloride

Molality	Osmotic Coefficient	Solution Partial Pressure, Mm. Hg	Solute Mean Molal Activity Coefficient	Solute Activity
0.7572	23.59	0.9390	0.20	0.02293
0.7399	23.43	0.9540	0.40	0.08759
0.7427	23.26	0.9730	0.60	0.1986
0.7556	23.08	0.9950	0.80	0.3654
0.7742	22.90	1.018	1.00	0.5995
0.7962	22.71	1.041	1.20	0.9130
0.8229	22.51	1.066	1.40	1.327
0.8524	22.30	1.091	1.60	1.860
0.8846	22.09	1.116	1.80	2.535
0.9202	21.87	1.142	2.00	3.387
0.9605	21.65	1.170	2.20	4.465
1.002	21.41	1.197	2.40	5.791
1.156	20.67	1.286	3.00	12.02
1.314	20.00	1.364	3.50	21.16
1.509	19.27	1.449	4.00	36.47
1.736	18.53	1.531	4.50	61.09
2.013	17.74	1.619	5.00	101.3
2.331	16.95	1.702	5.50	164.3
2.717	16.12	1.791	6.00	265.9
3.176	15.2	1.88	6.50	426.2
3.702	14.4	1.96	7.00	671.7
4.329	13.6	2.05	7.50	1054
5.090	12.8	2.14	8.00	1658
5.912	12.0	2.22	8.50	2525
6.946	11.2	2.31	9.00	3909
8.095	10.4	2.39	9.50	5914
9.378	9.77	2.46	10.0	8796
10.87	9.09	2.53	10.5	13040
12.52	8.45	2.60	11.0	18980
14.34	7.857	2.67	11.5	27220
16.37	7.296	2.73	12.0	38630
18.57	6.779	2.78	12.5	53900
20.87	6.310	2.83	13.0	73650
23.44	5.864	2.87	13.5	100100
26.11	5.459	2.91	14.0	133600
28.94	5.086	2.95	14.5	176100
31.81	4.750	2.97	15.0	227700
34.85	4.437	3.00	15.5	291800
37.82	4.160	3.02	16.0	366300
40.77	3.910	3.03	16.5	452500
43.74	3.681	3.04	17.0	553000
46.74	3.469	3.05	17.5	669100
49.82	3.271	3.05	18.0	804400
52.98	3.085	3.06	18.5	960800
56.20	2.911	3.06	19.0	1140000
59.24	2.757	3.06	19.5	1334000
62.29	2.613	3.06	20.0	1552000

Sodium Chloride

Molality	Osmotic Coefficient	Solution Partial Pressure, Mm. Hg	Solute Mean Mole Activity Coefficient	Solute Activity
0.20	0.9245	23.59	0.7347	0.02159
0.40	0.9203	23.44	0.6932	0.07689
0.60	0.9230	23.28	0.6732	0.1631
0.80	0.9288	23.12	0.6628	0.2812
1.00	0.9355	22.96	0.6572	0.4319
1.20	0.9428	22.80	0.6546	0.6172
1.40	0.9513	22.64	0.6548	0.8406
1.60	0.9616	22.47	0.6578	1.107
1.80	0.9723	22.30	0.6623	1.421
2.00	0.9833	22.13	0.6680	1.785
2.20	0.9948	21.95	0.6750	2.205
2.40	1.0068	21.77	0.6832	2.689
3.00	1.0453	21.21	0.7140	4.589
3.50	1.0796	20.73	0.7460	6.818
4.00	1.1158	20.22	0.7836	9.826
4.50	1.1531	19.70	0.8264	13.82
5.00	1.1916	19.16	0.8745	19.12
5.50	1.2309	18.61	0.9280	26.05
6.00	1.2706	18.04	0.9869	35.06
7.00	1.34	16.9	1.11	60.7
8.00	1.41	15.7	1.26	102
9.00	1.48	14.6	1.41	163
10.0	1.53	13.6	1.56	246
11.0	1.57	12.7	1.72	360
12.0	1.60	11.8	1.86	502
13.0	1.61	11.1	1.99	670
14.0	1.62	10.4	2.09	862
15.0	1.61	9.90	2.18	1070
16.0	1.60	9.40	2.24	1290
17.0	1.59	8.97	2.28	1510
18.0	1.56	8.59	2.31	1730
19.0	1.54	8.22	2.33	1970
20.00	1.52	7.91	2.34	2210

Potassium Chloride

Molality	Osmotic Coefficient	Solution Partial Pressure, Mm. Hg	Solute Mean Mole Activity Coefficient	Solute Activity
0.20	0.9130	23.600	0.7189	0.02067
0.40	0.9017	23.449	0.6666	0.07111
0.60	0.8976	23.299	0.6374	0.1462
0.80	0.8970	23.149	0.6184	0.2447
1.00	0.8974	23.000	0.6046	0.3656
1.20	0.8986	22.85	0.5942	0.5084
1.40	0.9010	22.70	0.5865	0.6742
1.60	0.9042	22.54	0.5808	0.8635
1.80	0.9081	22.39	0.5766	1.077
2.00	0.9124	22.24	0.5736	1.316
2.20	0.9168	22.09	0.5715	1.581
2.40	0.9214	21.93	0.5701	1.872
3.00	0.9367	21.46	0.5698	2.922
3.50	0.9504	21.07	0.5726	4.017
4.00	0.9647	20.67	0.5775	5.337
4.50	0.9795	20.26	0.5842	6.912
5.00	0.9950	19.85	0.5925	8.778
6.00	1.02	19.0	0.613	13.5
7.00	1.06	18.1	0.638	20.0
8.00	1.09	17.3	0.667	28.5
9.00	1.12	16.5	0.693	39.0
10.0	1.13	15.7	0.716	51.3
11.0	1.14	15.0	0.730	64.6
12.0	1.14	14.4	0.739	78.8
13.0	1.13	13.9	0.743	93.3
14.0	1.10	13.4	0.739	107
15.0	1.10	13.0	0.731	120
16.0	1.08	12.7	0.717	132

from Osmotic Coefficient Data

Molality	Osmotic Coefficient	Solution Partial Pressure, Mm. Hg	Solute Mean Molal Activity Coefficient	Solute Activity
		Cesium Chloride		
0.20	0.897	23.60	0.6953	0.01933
0.40	0.875	23.45	0.6288	0.06326
0.60	0.864	23.31	0.5899	0.1252
0.80	0.859	23.17	0.5640	0.2036
1.00	0.857	23.03	0.5453	0.2974
1.20	0.856	22.89	0.5307	0.4056
1.40	0.856	22.75	0.5190	0.5281
1.60	0.857	22.61	0.5097	0.6651
1.80	0.859	22.46	0.5022	0.8174
2.00	0.862	22.32	0.4964	0.9858
2.20	0.865	22.18	0.4915	1.169
2.40	0.869	22.03	0.4878	1.370
3.00	0.881	21.59	0.4800	2.074
3.50	0.891	21.23	0.4764	2.780
4.00	0.901	20.86	0.4746	3.603
4.50	0.912	20.49	0.4745	4.560
5.00	0.922	20.12	0.4751	5.644
5.50	0.932	19.74	0.4766	6.872
6.00	0.944	19.37	0.4798	8.287
6.50	0.955	18.99	0.4831	9.862
7.00	0.965	18.62	0.4865	11.6
7.50	0.976	18.24	0.4909	13.6
8.00	0.988	17.86	0.4962	15.8
8.50	0.996	17.51	0.5000	18.1
9.00	1.004	17.15	0.5040	20.6
9.50	1.009	16.81	0.5067	23.2
10.0	1.013	16.49	0.5090	25.9
10.5	1.016	16.17	0.5109	28.8
11.0	1.018	15.86	0.5123	31.8
12.0	1.012	15.3	0.510	37.4
13.0	0.999	14.8	0.503	42.9
14.0	0.979	14.4	0.493	47.7
15.0	0.955	14.1	0.480	52.0
		Rubidium Chloride		
0.20	0.907	23.60	0.7092	0.02012
0.40	0.893	23.45	0.6525	0.06812
0.60	0.887	23.30	0.6202	0.1384
0.80	0.886	23.15	0.5996	0.2301
1.00	0.885	23.01	0.5839	0.3409
1.20	0.886	22.86	0.5724	0.4718
1.40	0.888	22.71	0.5636	0.6227
1.60	0.890	22.56	0.5564	0.7927
1.80	0.893	22.41	0.5510	0.9839
2.00	0.896	22.27	0.5466	1.195
2.20	0.900	22.12	0.5435	1.429
2.40	0.903	21.97	0.5404	1.682
3.00	0.916	21.51	0.5365	2.591
3.50	0.928	21.13	0.5365	3.526
4.00	0.941	20.74	0.5388	4.645
4.50	0.953	20.35	0.5421	5.953
5.00	0.966	19.96	0.5466	7.471
6.00	0.995	19.1	0.560	11.3
7.00	1.02	18.3	0.578	16.4
8.00	1.05	17.5	0.599	23.0
9.00	1.07	16.7	0.617	30.9
10.0	1.09	16.0	0.633	40.1
11.0	1.10	15.3	0.643	50.1
12.0	1.09	14.7	0.647	60.3
13.0	1.08	14.2	0.645	70.4
14.0	1.07	13.8	0.640	80.4
15.0	1.05	13.4	0.631	89.8
16.0	1.03	13.1	0.618	97.9
17.0	1.00	12.8	0.603	105

with reasonable confidence, since ratios of properties of simple compounds, such as the alkali halides, seldom show abrupt changes or singularities. Data on osmotic coefficients were then plotted as shown in Figure 2, with the extrapolation being indicated by dashed lines.

A computer program was next written for the Burrough's 220 Compiler using values for the osmotic coefficients of the alkali chlorides in aqueous solution at 25° C. The data of Robinson and Stokes (2) and extrapolated values as obtained before were employed. The activity of water, α_1, was computed using the relationship (*1*)

$$a_1 = \exp - \left(\frac{\phi \nu m M_1}{1000} \right) \tag{1}$$

where ϕ is the solution osmotic coefficient, ν the number of ions per molecule of solute, m the solution molality, and M_1 the solute molecular weight.

From thermodynamic considerations the activity of a solvent is related to its partial pressure, p, and vapor pressure, p_0, (*1*) by

$$\ln a_1 = \ln \left(\frac{p}{p_0} \right) - \int_p^p \frac{\alpha}{RT} dp \tag{2}$$

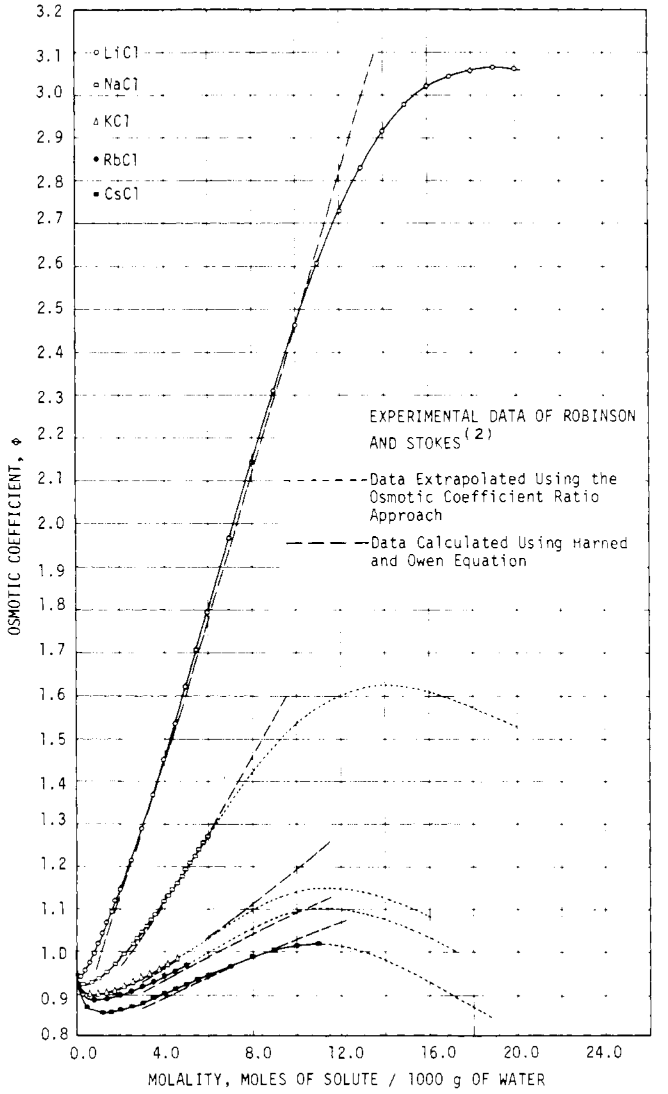

Figure 2. Experimental osmotic coefficients for alkali chlorides in aqueous solutions at 25° C. and guided extrapolation using osmotic coefficient ratios

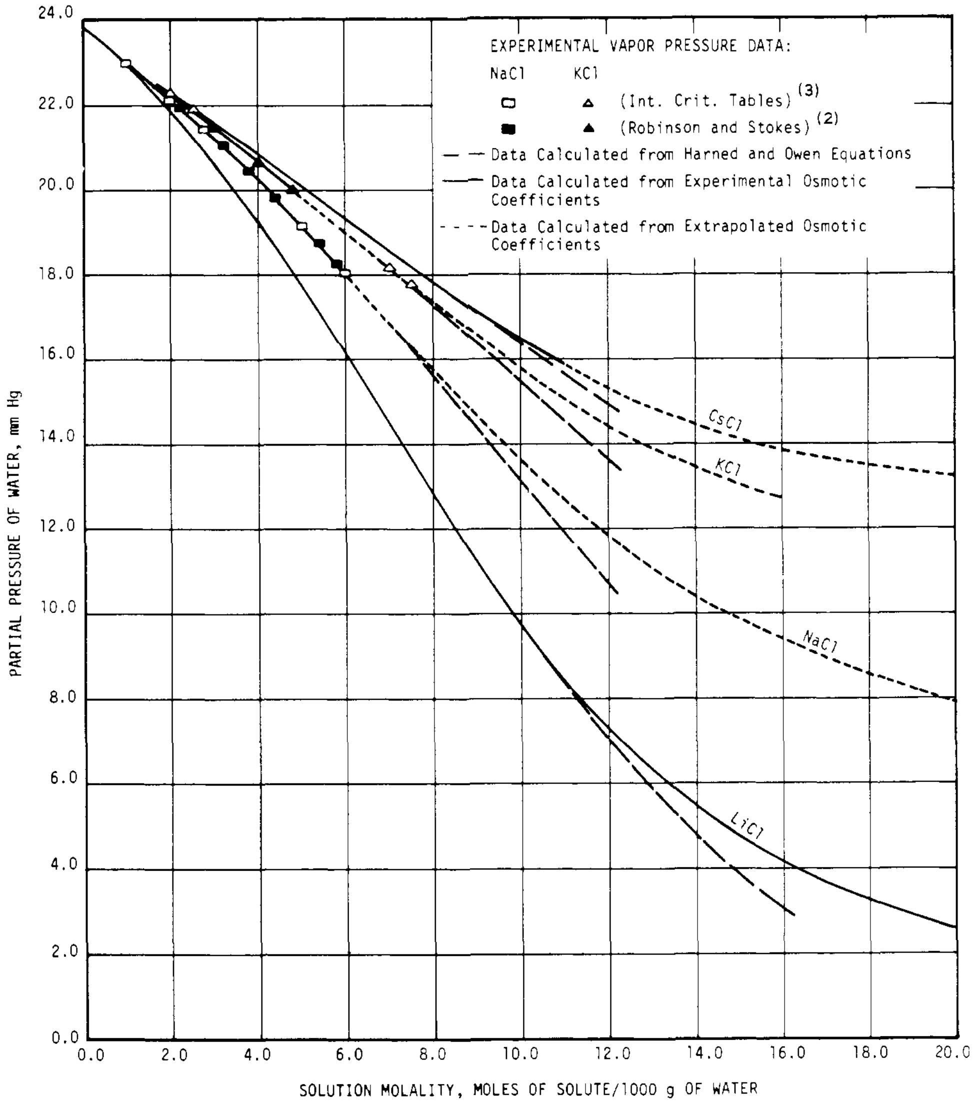

Figure 3. Vapor pressure of aqueous solutions of alkali chlorides at 25° C.

where α is the coefficient of compressibility of the solution. However, the term containing α is usually neglected as being smaller than the experimental error in vapor pressure measurements. Therefore, an acceptable approximation of Equation 2 is:

$$a_1 = p/p_0 \tag{3}$$

where p_0 has a value of 23.7560 mm. of mercury in the case of water at 25.0° C. Equation 3 was used to calculate the vapor pressure of the solution.

Figure 3 presents the experimental data for the vapor pressure of NaCl and KCl (*2*, *3*). It gives also curves for LiCl, KCl, and CsCl as computed using the osmotic coefficient approach and the Harned and Owen equation (*1*). It is considered very significant that the data obtained from the extrapolated osmotic coefficients of KCl predict with remarkable accuracy the data for supersaturated KCl solutions as reported in the International Critical Tables (*3*).

A numerical integration procedure was used to calculate activity coefficients and the activities of the electrolytes from the Gibbs-Duhem relationship written in the form (*1*)

$$d(\ln \gamma_\pm) = -\frac{1}{M}\, d[m(1-\phi)] \tag{4}$$

where $\gamma_\pm$ is the mean molal activity coefficient of the electrolyte. Rearranging Equation 4 and integrating yields:

$$\gamma_\pm = (\gamma_\pm)_0 \exp\left[\phi - \phi_0 - \int_{m_0}^{m} \frac{1-\phi}{m}\, dm\right] \tag{5}$$

The activity of the solute a_2 was then computed from:

$$a_2 = (\gamma_\pm m)^\nu \tag{6}$$

where ν is the total number of ions produced upon complete ionization of the solute molecule. Table I presents the results. The values obtained agree within 0.1% or better with experimental data where available. The authors estimated that the extrapolated values beyond the point of saturation are accurate to three significant figures at least to a concentration of 12 molal.

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Thermal Conductivity of Gaseous Air at Moderate and High Pressures

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Values of the thermal conductivity of air have been established for temperatures to 800° K. and pressures to 1000 atm. Reported thermal conductivity values for air at atmospheric pressure were related to temperature. Thermal conductivity values for nitrogen were used to establish a relationship between the reduced residual thermal conductivity, $(k - k^*)\lambda$, and reduced density. This relationship enabled thermal conductivity values to be established for gaseous air for a complete range of temperatures and pressures. The values from this study were compared with those resulting from a recent Russian investigation.

VALUES of the thermal conductivity of gaseous air are required for many design applications. Only meager experimental thermal conductivity data are available for this substance for the dense gaseous region. Granet and Kass (*8*) have used the generalized correlation of Gamson (*6*) to develop a plot of the thermal conductivity of air as a function of temperature and pressure for pressures to 2000 p.s.i.a. In a recently translated Russian book on the thermal conductivity of gases and liquids, Tsederberg (*25*) presented calculated values of the thermal conductivity of air for temperatures to 1000° C. and pressures to approximately 200 atm. In the present study, an alternate analysis based on the theorem of corresponding states has been used to establish values of the thermal conductivity of air for temperatures to 800° K. and pressures to 1000 atm. A similar study on the viscosity of gaseous air has recently been reported by Lo, Carroll, and Stiel (*17*).

THERMAL CONDUCTIVITY OF AIR AT MODERATE PRESSURES

Keyes (*16*) fitted the available data for the thermal conductivity of gaseous air at moderate pressure (approximately 1 atm.) for the temperature range 90° to 584° K. to the equation

$$k^* = \frac{0.632 \times 10^{-5}\,[T]^{1/2}}{1 + \frac{245}{T} \times 10^{-12/T}} \qquad (1)$$

Hilsenrath *et al.* (*12*) tabulated values of the thermal conductivity of air calculated from Equation 1 for temperatures from 80° to 1000° K. They assessed the reliability of the calculated values as being within 4%; however, the values for 590° to 1000° K. involved an extrapolation of Equation 1 beyond the range of the data utilized in its development. Glassman and Bonilla (*7*) found that their experimental values of the thermal conductivity of air for temperatures to 730° K. agreed with values calculated from Equation 1 to within 1% over the region investigated. Vines (*28*) measured thermal conductivity values for air from temperatures from 240° to 900° C. and found that the experimental values were in substantial agreement with the tabulated values of Hilsenrath *et al.* for temperatures to 750° C. but were slightly higher for temperatures above 750° C.