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### Literature Cited

(1) Beaudry, B. J., *J. Less-Common Metals*, **14**, 370 (1968).
(2) Bredig, M. A., "Molten Salt Chemistry," M. Blander, Ed., Interscience, New York, N.Y., 1964, p 367.
(3) Corbett, J. D., "Fused Salts," B. Sundheim, Ed., McGraw-Hill, New York, N.Y., 1964, p 341.
(4) Corbett, J. D., Pollard, D. L., Mee, J. E., *Inorg. Chem.*, **5**, 761 (1966).
(5) Dworkin, A. S., Bronstein, H. R., Bredig, M. A., *J. Phys. Chem.*, **72**, 1892 (1968).
(6) Dworkin, A. S., Bredig, M. A., *J. Phys. Chem.*, **75**, 2340 (1971).
(7) Polyachenok, O. G., Novikov, G. I., *Russ. J. Inorg. Chem.*, **8**, 1478 (1963).

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# Surface Tension of LiCl–KCl Eutectic Mixture

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**The surface tension of the eutectic composition of the binary molten salt system LiCl-KCl has been measured over the temperature range 375–600°C.**

Even though the molten eutectic mixture of lithium and potassium chloride has been used extensively as a solvent in both electrochemical and chemical studies, very little is known of its physical properties—e.g., surface tension, viscosity. As a consequence of studying the binary molten salt system LiCl–KCl, we have measured the surface tension of the eutectic, and report our findings in this paper.

Of the numerous methods for determining the surface tension of molten salts, the maximum bubble pressure method was chosen for this investigation. This technique has been used to measure the surface tension of molten salts by numerous workers, and the theory and practice of this method have been extensively reviewed by Dahl *(3)*.

## Experimental

The experimental details were essentially the same as those of Dahl and Duke *(4)* with the exception that the capillary was fabricated from pure gold and was 2.25 cm long with an orifice approximately 0.8 mm in diam. All measurements were made in a purified argon atmosphere on carefully purified salts. The temperature of the melt was measured with a chromel-alumel thermocouple and was maintained constant within ±0.5°C. The furnace was arranged in such a manner that the vertical temperature gradient of the melt was less than 1.0°C. A more detailed discussion of the experimental technique is given elsewhere *(8)*.

Both the lithium chloride and potassium chloride used in these experiments were of analytical reagent purity and were carefully vacuum-dried before use. The eutectic composition was made up by accurately weighing the dried materials directly into the container and, after the salts were melted, they were further purified by the use of chlorine and hydrogen chloride gas *(7)*. All weighing and other manipulations of the dried salts were done in an atmosphere whose water content was less than 100 ppm.

The exact composition of the eutectic in the LiCl–KCl system is a matter of some controversy *(1)*. For this work the eutectic composition was determined with the aid of a hot-stage microscope. A number of possible eutectic compositions were examined to obtain a sample exhibiting the eutectic properties. The composition of this sample was then determined by analyzing for both lithium and potassium by atomic absorption. Our results agree with those of Plyushchev and Kovalev *(9)*; the eutectic in this system lies at 41.8 ± 0.3 mol % KCl–58.2 ± 0.3 mol % LiCl and has a melting point of 352° ± 1°C.

Prior to determining the surface tension of the LiCl–KCl eutectic, we measured the surface tension of both $NaNO_3$ and $KNO_3$, and the agreement between our results and the accepted literature values *(5)*, shown in Table I, is quite good.

In all our calculations of the surface tension, appropriate correction was made for expansion of the capillary orifice *(2)*.

## Results and Discussion

A total of 35 determinations of the surface tension of the eutectic LiCl–KCl mixture was made at different depths of immersion of the capillary and at various temperatures between 375° and 600°C. The resulting surface tension could be expressed as a linear function of the temperature by an expression of the form:

$$\gamma = 165.3 - 0.0780\,t$$

The standard deviation in these experiments was 0.2 dyn/cm. In calculating the surface tension, the density values of Van Artsdalen and Jaffee *(10)* were used.

To the best of our knowledge, the only other measurement of the surface tension of the LiCl–KCl system was that of Jaeger *(6)* at 447°C on the composition 40.5 mol % KCl–59.5 mol % LiCl, which is approximately the eutectic composition. His value of 123.6 dyn/cm is about 5% lower than our value, 130.4 dyn/cm.

While the surface tension does change with composition, the discrepancy between our results and those of Jaeger's cannot be accounted for on that basis. Measurements of the surface tension of other compositions in

**Table I. Surface Tension Values for $NaNO_3$ and $KNO_3$**

| Salt | $\gamma$ (lit.) (dyn/cm at $t$°C) | $\gamma$ (exptl) (dyn/cm at $t$°C) |
|---|---|---|
| $NaNO_3$ | $136.1 - 0.0573\,t$ | $138.8 - 0.0613\,t$ |
| $KNO_3$ | $137.3 - 0.0727\,t$ | $136.5 - 0.0705\,t$ |

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the LiCl-KCl system *(8)* indicate that the slight difference in composition between our melt and that of Jaeger's (42 mol % KCl vs. 40.5 mol % KCl) would result in a change in surface tension of less than 0.5%.

### Literature Cited

(1) Clark, P. V., "Physical Properties of Fused Salt Mixtures," Vol 1, p 129, SC-RR-65-930, Sandia Laboratories, Albuquerque, N.M., June 15, 1965.
(2) Clark, S. P., "Handbook of Physical Constants," p 78, Geological Soc. of America, New York, N.Y., 1966.
(3) Dahl, J. L., "Surface Tension of Some Binary Fused Salt Systems," PhD thesis, Iowa State College, 1957.
(4) Dahl, J. L., Duke, F. R., *J. Phys. Chem.*, **62**, 1498 (1958).
(5) Janz, G. J., Dijkhuis, C. G. M., "Molten Salts," Vol 2, pp 93-4, U.S. Dept. of Commerce, National Bureau of Standards, 1969.
(6) Jaeger, F. M., *Z. Anorg. Chem.*, **101**, 1 (1917).
(7) Nissen, D. A., *J. Inorg. Nuclear Chem.*, **28**, 1740 (1966).
(8) Nissen, D. A., Carlsten, D. A., unpublished results, 1972.
(9) Plyuschchev, V. E., Kovalev, F. V., *Zh. Neorg. Khim.*, **1**, 1013 (1956).
(10) Van Artsdalen, E. R., Jaffee, I. S., *J. Phys. Chem.*, **59**, 1181 (1955).

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# Thermodynamic Properties of Neopentane

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**The effect of pressure on the enthalpy and entropy of 2,2-dimethylpropane (neopentane) was evaluated numerically from experimental *PVT* data. The resulting values were used in conjunction with ideal state properties from the literature to construct the Mollier diagram for the temperature range of 620–900°R and for pressures up to 4500 psia.**

The development of the fundamental equations employed in the evaluation ot the enthalpy and entropy were presented by Hsu and McKetta (*3*). These relationships, Equations 1–6, use the volume residual concept:

$$\Delta H_{P,T} = \Delta H_T^\circ + H_P + (\Delta H_v)_{T_0} \tag{1}$$

$$\Delta S_{P,T} = \Delta S_T^\circ + S_P + (\Delta S_v)_{T_0} \tag{2}$$

$$\Delta H_T^\circ = \int_{T_0}^{T} C_P^\circ\, dT \tag{3}$$

$$\Delta S_T^\circ = \int_{T_0}^{T} \frac{C_P^\circ}{T}\, dT \tag{4}$$

$$H_P = J\left\{\int_0^P\left[T\left(\frac{\partial \gamma}{\partial T}\right)_P - \gamma\right]_T dP - \int_0^{P_0}\left[T\left(\frac{\partial \gamma}{\partial T}\right)_P - \gamma\right]_{T_0} dP\right\} \tag{5}$$

$$S_P = J\int_0^P\left[\left(\frac{\partial \gamma}{\partial T}\right)_P\right]_T dP - R\ln(P/P_0) - J\int_0^{P_0}\left[\left(\frac{\partial \gamma}{\partial T}\right)_P\right]_{T_0} dP \tag{6}$$

The experimental *PVT* data (*2*) were smoothed and interpolated by the least-squares method of Lin (*4*) into an evenly spaced array of pressure, temperature, and volume residual. Values were selected from regions of this array to evaluate constants in a localized equation of state,

$$\gamma = C_1 + C_2P + C_3P^2 + C_4T + C_5PT + C_6P^2T + C_7T^2 + C_8PT^2 + C_9P^2T^2 \tag{7}$$

which was used analytically in Equations 5 and 6 to evaluate the derivatives and the pressure integrals by integration over subintervals with 5 psi increments. Details of these calculations were presented by Lin (*4, 5*).

The change in fugacity coefficient for each pressure increment was evaluated by substituting Equation 7 into:

$$\nu_2 = \nu_1 \exp\left(\frac{-1}{RT}\int_{P_1}^{P_2} \gamma\, dP\right) \tag{8}$$

Specific volumes were similarly found by using Equation 7 in the following definition of the volume residual:

$$V = RT/P - \gamma(T,P) \tag{9}$$

### Reference State

The saturated liquid at 620°R was taken as the reference state—i.e., $\Delta H_{P,T} = 0$ and $\Delta S_{P,T} = 0$, for evaluation of the enthalpies and entropies presented here. The vapor pressure of neopentane at this temperature was 87.61 psia as calculated from the Nernst equation reported by Dawson et al. (*2*).

### Sources of Data

The experimental volumetric data used to evaluate the enthalpies and entropies presented here were taken from the work of Dawson et al. (*1, 2*). Saturated state densities, heats of vaporization, and vapor pressures were calculated from correlations in the same work.

The isobaric integrations required in Equations 3 and 4 were performed at zero pressure using the ideal state heat capacities reported by Pitzer and Kilpatrick (*6*). To allow analytical integration, the equation of Yuan and Mok (*7*) was used,

$$C_p^\circ = 15.4496 + 92.6474\exp(-571.7382/T) \tag{10}$$

where *T* is the temperature, K. The constants in Equation 10 were evaluated by an iterative least-squares method using the data of Pitzer and Kilpatrick. The standard error of the regression was 0.088 Btu/lb °R and the average absolute deviation was 0.035 Btu/lb °R. Furthermore, the maximum deviation of reported heat capacity data from those calculated by Equation 10 was less than the error in the original data. This equation was substituted into Equations 3 and 4, and the integrations were performed

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