# Mutual Solubilities of Benzene and Water

## Equilibria in the Two Phase Liquid–Liquid Region

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**The mutual solubilities in the liquid–liquid benzene–water system were studied from 100 to 460° F. at pressures of 1000 and 5000 p.s.i.g. The densities of the saturated liquid phases were also obtained. The phase-contacting apparatus consisted of an insulated high pressure cell with provisions for heating, pressurizing, sampling, and temperature and pressure measurements. The liquid–liquid system under study was contained in the cell by a moveable piston. Measurement of the piston motion provided data for calculation of density. To avoid emulsification problems, the equilibrium cell was not agitated, which resulted in the use of a lengthy equilibration period (24 hours). The solubility results are generally in good agreement with results that are available from other studies at different pressure and temperature conditions. The densities of the saturated phases are almost identical to pure solvent densities at low temperatures, but differ appreciably at high temperatures where the high solubilities have a strong influence on density.**

ALTHOUGH a substantial amount of benzene–water mutual solubility data is available in the literature (*1, 3–7, 10–13, 15, 16, 19–22*), most of the data are limited to moderate temperatures and pressures, and many of the results are conflicting. This study (*23*) was undertaken to obtain liquid–liquid mutual solubility data at higher temperatures and pressures (up to 460° F. and 5000 p.s.i.g.), and to lay groundwork for subsequent solubility studies up to the critical solution conditions for the benzene– water system.

## APPARATUS

The phase-contacting equipment consisted of a high-pressure cylinder fitted with a moveable piston for confining the benzene–water mixtures, and auxiliaries for sampling, pressure and thermal regulation, and for pressure, volume, and temperature measurement. The assembly is shown diagramatically in Figure 1 while detailed information is available (*23*).

Nitrogen was hydraulically compressed in vessel I by fluid supplied from air-driven pump *E*. The pressure on the nitrogen was transmitted to distilled water (*S*) and in turn to the piston in equilibrium cell *X*. Water was employed for pressurizing cell *X* to avoid the possibility for trace contamination. Pressures were indicated on gages *J* and *U* and recorded via pressure transducer *V*. All gages were calibrated by dead-weight test gage and were accurate to about 25 p.s.i.

Since the equilibrium cell *X* was a smooth-bore cylinder, differential volumes could be calculated from measurements of the piston movement during sampling. Such measurements were gained from linear-variable-differential transformer *Y* (*18*) and machinists gage *Z*. The volume of a sample was measured to within 0.03 cc. The discharged sample was collected in chilled flask *DD* and weighed by analytical balance.

## MATERIALS

The benzene used in this study was the pure grade (99 mole per cent minimum-purity) supplied by Phillips Petroleum Co. Several samples were analyzed by standard gas chromatographic procedures and found to be essentially pure, since no other peaks appeared at maximum chromatograph sensitivity. Accordingly, the benzene was not further purified. The water was taken from the laboratory distilled water supply and redistilled in the absence of carbon dioxide in a simple batch still. Both materials were dispensed as required in the investigation from sealed vessels in which a nitrogen atmosphere was maintained.

## PROCEDURE

For charging, the equilibrium cell was removed from the phase-contacting equipment, and both closures and the piston were removed. After cleaning the parts and inserting the piston, about 70-ml. each of water and benzene were withdrawn from storage and poured into the sample end of the cell so it was slightly overfilled and some liquid was forced out when the closure was screwed on. The other (pressurizing) end of the cell was filled with distilled water and closed. The charged cell was then installed in the phase-contacting equipment.

After filling surge cell *S* with distilled water and pressurizing the system to about 200 p.s.i. with nitrogen, the connections on tee *W* were slightly loosened to bleed out air and leave a continuous water couple between the water-surge cell *S* and the equilibrium-cell piston. Also, a portion of the charge was bled through the sampling valve to purge gases from the sampling lines.

With the equilibrium cell in the horizontal position, the system was pressurized by admitting nitrogen from cylinder *K*, and compressing the nitrogen by pumping oil into the system with pump *E*. During the heating period, the expansion of the cell charge was followed with the volume-measuring equipment to assure free piston motion. In some cases, nitrogen was vented from the system to relieve the pressure increase caused by the charge expansion.

After reaching the operating temperature and pressure, the cell normally remained in the horizontal position without agitation for a minimum of 24 hours. The cell assembly was then gently rotated into the vertical position and normally remained in this position for three hours to assure complete phase separation. With the sampling line and sample flask attached, valve *AA* was opened slightly and samples were drawn off at a rate less than 3-ml. per minute. The pressure on the piston was held constant

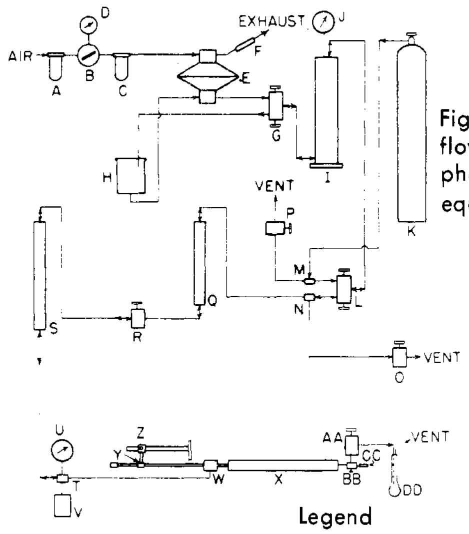

Figure 1. Simplified flow diagram of the phase–contacting equipment

Legend

*A* = air filter
*B* = air diaphragm valve
*C* = air lubricator
*D* = air pressure gage, 0–160 p.s.i.
*E* = sprague pump
*F* = muffler
*G* = double valve for hydraulic fluid
*H* = hydraulic fluid reservoir
*I* = high pressure cell
*J* = nitrogen pressure gage, 0–10,000 p.s.i.
*K* = nitrogen cylinder
*L* = double valve for nitrogen
*M, N* = tee
*O, P* = let-down valve
*Q* = high pressure nitrogen surge cell
*R* = valve
*S* = high pressure water surge cell
*T* = cross
*U* = water pressure gage, 0–10,000 p.s.i.
*V* = pressure transducer, 0–5,000 p.s.i.
*W* = tee
*X* = equilibrium cell
*Y* = linear variable differential transformer, *LVDT*
*Z* = vernier height gage
*AA* = sampling valve
*BB* = tee
*CC* = thermocouple
*DD* = sampling flask

by pump *E*. With the low sampling rate, enough cooling occurred in the sampling line that very little liquid was flash-vaporized in the Kjeldahl flask, and this small amount was effectively condensed in the bulb of the flask.

A sample of about 20-ml. was taken from both of the liquid phases in each experiment, and the upper, middle (interfacial), and lower portions of the charge were discarded. At the beginning and end of each sample, the vernier height gage reading was taken with the *LVDT* centered over its core. The difference between these values (the sample displacement) was converted with a calibration factor to give the volume that the sample occupied under the operating conditions.

After the cell charge had been completely withdrawn, valve *AA* was opened with full pressure on the piston to assure that the seal between the piston and the cell was intact.

## ANALYSIS

The benzene-rich phase was analyzed for water by the Fischer method (*8*) using a potentiometric end-point (*2*). The sample, which had become heterogeneous after reducing the temperature from the higher equilibrium value, was made homogeneous by adding a weighed amount of standard water-in-methanol solution. A weighed portion of the liquid was analyzed, and the solubility was calculated with an allowance for the water added in the methanol standard solution.

The water-rich phase was analyzed for benzene by slowly vaporizing the sample into a purified air stream, passing the vapors over copper oxide at 1450-1500° F., absorbing the resulting carbon dioxide in a known volume of standard sodium hydroxide solution, and determining the amount of sodium hydroxide that was not used to react with the carbon dioxide. The determination of unreacted sodium hydroxide was made by titrating with standard hydrochloric acid after precipitating the carbonates with excess barium chloride.

For both phases, the filled and empty sample flasks were weighed on an analytical balance to give the total sample weight by difference. Phase densities were then calculated using the sample volumes determined earlier.

**Calibration of Cell Volume.** The volume of the cell was calibrated by charging the cell with pure degassed water, and drawing off samples at various temperatures and pressures. The piston displacement for each sample was obtained by the difference between the height gage readings. After smoothing the experimental results to even temperature, the corresponding volumes were calculated from the weights of the water samples using specific volume data from Keenan and Keyes (*14*). In this way, conversion factors (cc. per linear inch of cell) for use in determining sample volumes were obtained that are functions of both temperature and pressure.

**Equilibration.** This work differs from almost all previous high-temperature solubility studies in that no agitation was used to help establish equilibrium rapidly. Here, agitation was avoided to preclude emulsion formation which could become a problem in subsequent work at temperatures nearer the critical solution temperature. In this study, the solute diffused through a solvent layer that remained stagnant after the initial heating period was completed. However, during the equilibration period, the cell was horizontal to provide a maximum interfacial area and minimum diffusive distance.

The approach to equilibrium in 24 hours for the dilute solutions was calculated for 100° F. using Fick's law and estimated (*24*) diffusivities. The boundary conditions used in the diffusion equation were: the solvent is uniformly saturated with solute after an infinitely long contact period; the solvent is always saturated with solute at the interface; the initial solute concentration in the solvent is zero; and the concentration gradient is always zero at the cell wall furthest from the interface. At 100° F., the diffusivity of benzene in water was taken as $6 \times 10^{-5}$ ft.$^2$ per hr; and that of water in benzene, $3 \times 10^{-4}$. A rectangular cross-section was chosen to simplify the calculations. It was found that the approach to equilibrium in 24 hours was more than 99.9 per cent for the water diffusing into the benzene, and about 92 per cent for the benzene in water. This predicted approach to equilibrium for benzene in water would be unacceptable if it did not represent the limiting minimum approach. However, in practice, such factors as thermal agitation during heating and enhanced diffusivities at elevated temperatures result in considerably higher rates of mass transfer.

A series of experiments was performed at 100° F. which verified that equilibrium was established in 24 hours. The results for benzene dissolved in water are illustrated in Figure 2, and a similar pattern was found for water dissolved in benzene.

## EXPERIMENTAL RESULTS

The experimental solubility and density results of this study are listed in Table I, and the smoothed results in

Table II. As indicated by asterisks, some data were discarded. Most of these poor results accumulated in the early developmental stages of the study due to poor sampling equipment and techniques. After reducing the sampling line volume and decreasing the sampling rate, both phases were successfully sampled without entraining a portion of the other liquid phase.

The solubility data are plotted on Figures 3 and 4. The water solubility line passes through all the experimental points for 1000 p.s.i.g., as does the benzene solubility curve at 5000 p.s.i.g. Although the points for water solubility at 5000 p.s.i.g. are scattered slightly, a line is well-defined. At 400° F., the line begins curving sharply as the critical solution temperature is approached. The worst data were obtained for the water phase at 1000 p.s.i.g. Since most of the 340 and 400° F. points were known to be high as a result of difficulties with irregularly high analytical blanks, the curve was drawn below them. The 5000 p.s.i.g. behavior was influential when drawing the 1000 p.s.i.g. curve.

Compared with solubility, the density data are scattered. However, although the results appear worse on the expanded scales of Figures 5 and 6, the average deviation of the points from the curve is less than one per cent of the density. In view of the secondary nature of these data, the reproducibility is considered satisfactory.

## COMPARISON OF SOLUBILITY RESULTS

Both liquid phases of the benzene-water system have been extensively studied at low temperatures by other investigators, and results at higher temperatures are available for the water phase. The results of this study are compared with the literature data in Figures 3 and 4.

In the benzene phase, the logarithm of solubility was found to be linear with reciprocal temperature which is typical for the solubility of water in hydrocarbons. An increase in pressure results in a uniform decrease in solubility such that the 5000 p.s.i.g. isobar is below and about parallel to the 1000 p.s.i.g. isobar. By extrapolation, the atmospheric pressure isobar should be parallel to this work, but at higher solubilities. This is in agreement with the results of Stavely, Jeffes, and Moy (*20*). The solubilities of Groschuff (*10*) and Hill (*12*) are also higher and almost parallel. Although the other data that are shown in Figure 3 do not correspond exactly, the over-all agreement of the results of this study with those of others is considered excellent for the benzene phase.

Typical temperature behavior for hydrocarbons was also observed in the water phase, where a 4000-p.s.i. pressure increase was found to cause a large increase in solubility. A proportionate change should be observed between this 1000-p.s.i.g. work and the low pressure work of others, but the change is very small. Nevertheless, if the two 100° F. points from this study were very slightly higher, the agreement with other low-temperature data would be excellent.

Table I. Experimental Solubility and Density Results

| | Benzene Phase | | Water Phase | |
|---|---|---|---|---|
| Temp., ° F. | Water concn., mole frac. × $10^4$ | Density, g./cc. | Benzene concn., mole frac. × $10^4$ | Density, g./cc. |
| | | 1000 P.S.I.G. | | |
| 100.3 | 48.7 | 0.865 | 4.34 | 0.993 |
| 100.1 | 46.6 | 0.861 | 4.54 | 0.992 |
| 99.9 | 41.6 | 0.856 | 4.33 | 0.994 |
| 99.9 | 41.8 | 0.858 | 4.61 | 0.991 |
| 101.5 | 43.3 | 0.859 | ...[a] | ... |
| 101.0 | 42.1 | 0.856 | 4.60 | 0.992 |
| 160.3 | 124 | 0.816 | 6.63 | 0.975 |
| 219.0 | 274 | 0.779 | 8.56 | 0.952 |
| 218.0 | ... | ... | 9.84 | 0.941 |
| 280.0 | 558. | 0.761 | *[b] | 0.913 |
| 280.3 | ... | ... | 14.3 | 0.920 |
| 281.0 | ... | ... | 18.6 | 0.922 |
| 340.0 | 1000 | 0.673 | 44.2†[c] | 0.859 |
| 339.3 | * | 0.686 | 42.7† | 0.905 |
| 339.3 | ... | 0.680 | 41.6† | 0.854 |
| 340.3 | ... | ... | 46.5† | 0.879 |
| 341.0 | ... | ... | 36.0† | 0.878 |
| 397.3 | 1770 | 0.641 | ... | ... |
| 396.3 | ... | ... | 85.3 | 0.815 |
| 399.7 | * | 0.575 | 81.0 | 0.830 |
| 398.0 | ... | 0.582 | 94.2† | 0.838 |
| 399.0 | ... | ... | 72.6 | 0.837 |
| | | 5000 P.S.I.G. | | |
| 100.3 | 38.1 | 0.885 | 5.61 | 1.005 |
| 161.0 | 105 | 0.848 | * | 0.988 |
| 159.7 | * | 0.851 | 8.95 | 0.987 |
| 160.3 | 110 | 0.850 | ... | ... |
| 219.7 | * | 0.812 | 14.1 | 0.966 |
| 220.7 | 263 | 0.820 | ... | 0.961 |
| 279.3 | 505 | 0.781 | 22.8 | 0.922 |
| 339.3 | 959 | 0.753 | 43.1 | 0.897 |
| 400.7 | 1530 | 0.713 | 98.3 | 0.867 |
| 460.7 | 4320 | 0.660 | 265 | 0.787 |
| 459.7 | 4600 | 0.664 | 248 | 0.790 |

[a] ... = No analysis was performed. [b] * = Discarded data. [c] † = Results known to be high due to a high analytical blank.

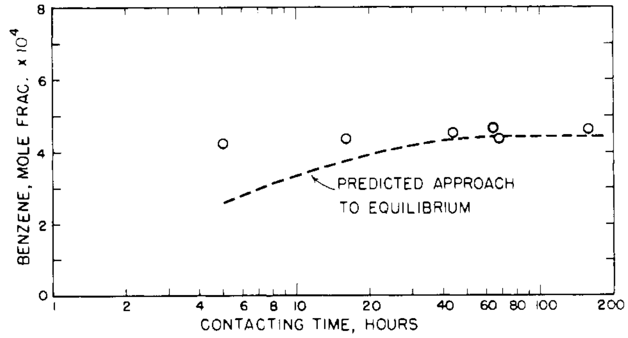

Figure 2. Benzene dissolved in water at 100° F. and 1000 p.s.i.g. as a function of contacting time

The high-temperature solubility results of Jaeger (*13*) required conversions and corrections for comparison with the solubilities from this study. In his pioneer work, Jaeger analyzed by simply measuring the volumes which separated after cooling the samples to room temperature. Accordingly room-temperature density data were used to convert the solubility results from the reported volumetric units. In addition, since Jaeger incorrectly assumed that the solubility of benzene in water at room temperature was negligible, 4 × $10^{-4}$ mole fraction units were added to each experimental solubility.

Since the pressure for the work of Jaeger increased with temperature, the results should converge on this work until intersection occurs with the 1000-p.s.i.g. curve at about 460° F. This behavior is not observed. Jaeger's results are lower than the results of this work for all temperatures. However, Jaeger's results for the xylenes are almost identically low when compared with the data of Pryor and Jentoft (*17*). Similar departures are observed in comparing the toluene data with that of Bohon and Claussen (*6*). Apparently, the 10-minute equilibration period used by Jaeger did not produce an equilibrium system.

The two isobars that were plotted in Figure 4 from the smoothed results of Kudchadker and McKetta (*15*) do not agree with this work or the work of others. These two isobars (for 60 and 450 p.s.i.a) indicate very unusual tem-

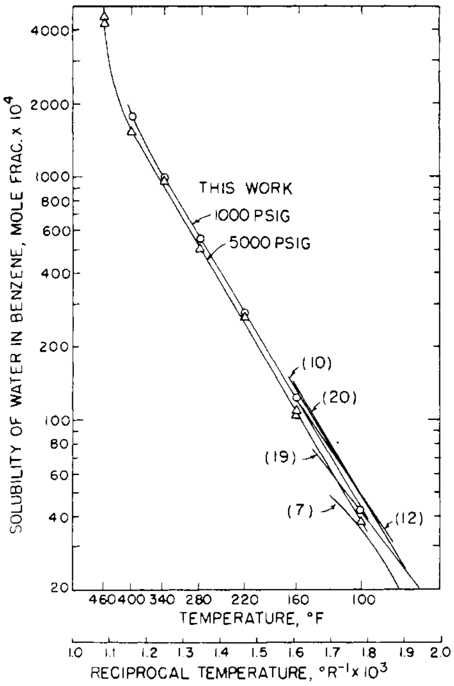

**Figure 3. Solubility of water in benzene**

The following work of others was performed at one atmosphere pressure or less: Clifford (*7*), Groschuff (*10*), Hill (*12*), Rosenbaum and Walton (*19*), and Stavely, Jeffes, and Moy (*20*).

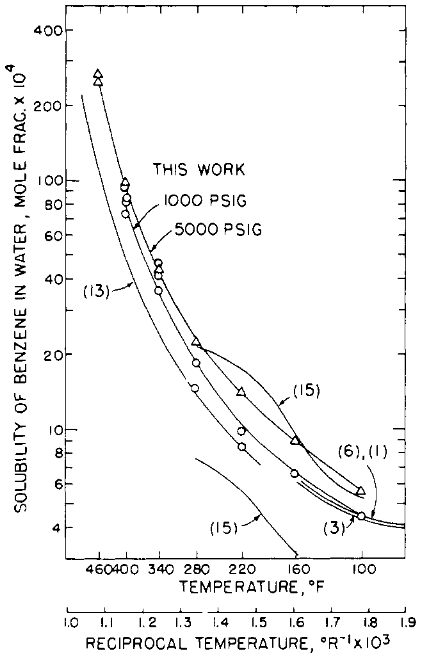

**Figure 4. Solubility of benzene in water**

The following work of others was performed at the vapor pressure of the system: Alexander (*1*), Arnold et al. (*3*), Bohon and Claussen (*6*), and Jaeger (*13*). Two curves are shown for the results of Kudchadker and McKetta (*15*), the upper for 450 p.s.i.a., and the lower, 60 p.s.i.a.

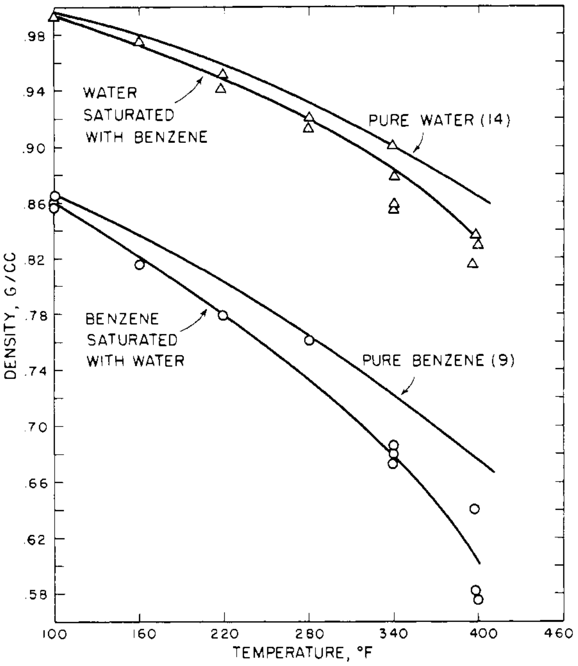

**Figure 5. Density of the saturated liquid phases at 1000 p.s.i.g.**

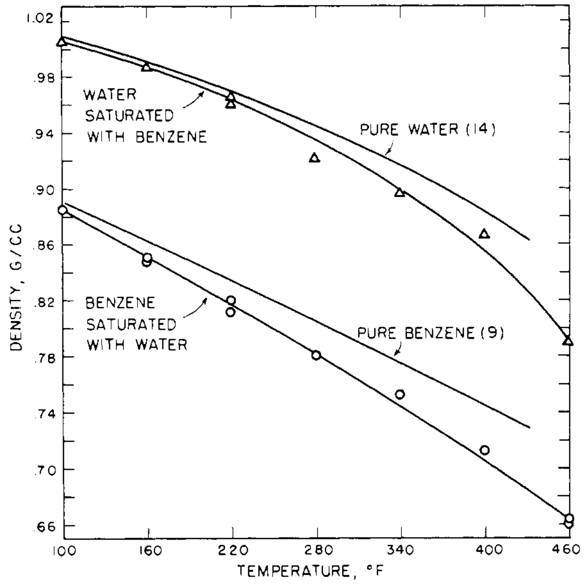

**Figure 6. Density of the saturated liquid phases at 5000 p.s.i.g.**

Table II. Experimental Solubility and Density Results

| | Benzene Phase | | | | Water Phase | | | |
|---|---|---|---|---|---|---|---|---|
| | Water concn. | | | | Benzene concn. | | | |
| Temp., °F. | Mole frac. x $10^4$ | Wt. frac. x $10^4$ | Moles/liter | Density, g./cc. | Mole frac. x $10^4$ | Wt. frac. x $10^4$ | Moles/liter | Density, g./cc. |
| | | | | 1000 P.S.I.G. | | | | |
| 100 | 42.3 | 9.78 | 0.0467 | 0.860 | 4.46 | 19.3 | 0.0246 | 0.993 |
| 160 | 121 | 28.2 | 0.129 | 0.821 | 6.65 | 28.8 | 0.0360 | 0.972 |
| 220 | 274 | 64.5 | 0.279 | 0.779 | 10.1 | 43.6 | 0.0530 | 0.948 |
| 280 | 558 | 134 | 0.544 | 0.732 | 18.6 | 80.1 | 0.0942 | 0.919 |
| 340 | 1000 | 250 | 0.944 | 0.679 | 36.0 | 154 | 0.174 | 0.881 |
| 400 | 1780 | 475 | 1.58 | 0.601 | 82.0 | 346 | 0.369 | 0.831 |
| | | | | 5000 P.S.I.G. | | | | |
| 100 | 38.1 | 8.80 | 0.0432 | 0.885 | 5.61 | 24.3 | 0.312 | 1.005 |
| 160 | 106 | 24.6 | 0.116 | 0.851 | 9.05 | 39.2 | 0.0495 | 0.987 |
| 220 | 245 | 57.5 | 0.261 | 0.817 | 14.1 | 60.8 | 0.0751 | 0.965 |
| 280 | 500 | 120 | 0.520 | 0.781 | 22.8 | 98.0 | 0.117 | 0.935 |
| 340 | 905 | 224 | 0.927 | 0.745 | 43.0 | 184 | 0.211 | 0.899 |
| 400 | 1620 | 445 | 1.74 | 0.706 | 98.0 | 411 | 0.449 | 0.855 |
| 460 | 4500 | 1590 | 5.83 | 0.663 | 255 | 1020 | 1.03 | 0.791 |

perature behavior as well as a very strong influence of pressure on solubility. The smoothed atmospheric pressure results were so low that they could not be plotted on Figure 4.

The density results are compared with data for the pure solvents in Figures 5 and 6. As shown, at low temperatures, the small amount of dissolved solute causes a small decrease in solvent density. As temperature increases, solubility increases, and the density departure becomes larger.

## ACKNOWLEDGMENT

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# Kinematic Viscosity of Liquid Rubidium from 67° to 688°C.

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**The kinematic viscosity of pure rubidium was measured from 67° to 688° C. in an all-metal capillary viscometer. The calibration of the apparatus without the use of a reference fluid is described, and experimental results are compared with low-temperature data for rubidium and with data for potassium and sodium. The correlated kinematic viscosity of rubidium, in centistokes, may be expressed in terms of temperature, in degrees Kelvin, as: log ($\mu/\rho$) = 250/$T$ − 1.15.**

THE ANTICIPATED USE of alkali metals as working fluids, heat transfer media, and lubricants in high-temperature energy-conversion systems has spurred considerable research on the thermophysical properties of these fluids. However, there are still many areas in which reliable data are meager or lacking. Experimental measurement of liquid alkali-metal viscosity is in progress in several laboratories, and new experimental data have been reported recently for potassium (*17*). The viscosities of cesium, potassium, sodium, and lithium have been measured at temperatures as high as 1150° C. (for potassium) by damped torsional oscillation methods (*1, 2, 8, 9, 17*), and that of sodium has been determined to 600° C. by capillary viscometry (*4, 5*). On the other hand, the experimental viscosity of rubidium has not been reported for temperatures above 220° C.

As part of an Air Force sponsored research program on the influence of contaminants in liquid alkali-metal systems, an all-metal capillary viscometer has been developed in this laboratory. Extensive viscosity measurements have been made on pure rubidium from 67° to 688° C., and it is the purpose of this paper to present the resulting experimental kinematic viscosity data.

## EXPERIMENTAL APPARATUS AND MATERIALS

**Rubidium Samples.** Two batches of pure rubidium were obtained commercially for use in this program. Cesium represented the major impurity in each batch, being present to the extent of 0.4 and 0.02 wt. per cent, respectively. The rubidium was analyzed for trace metal constituents by emission spectroscopy; for alkali metals