Densities and Electrical Conductivities of Oleums

RICHARD POPIEL
Bell Telephone Laboratories, Inc., Murray Hill, N. J.

Improved techniques and rigid analytical controls have been employed to surmount the difficulties encountered in obtaining density and conductivity data for various oleum compositions. The measurements cover the full oleum composition range from pure sulfuric acid to liquid anhydrous sulfur trioxide.

ANY UNDERSTANDING of the constitution of oleums depends upon the availability of accurate data. Such data, for various physical properties, are often nonexistent. For example, accurate density data for the entire composition range of oleums at 25° C. have been unavailable. Knietsch (4) measured specific gravities at 35° C. for the entire range. In certain concentration ranges excellent precision was apparently obtained, but lack of precision was evident elsewhere.

Many years later, Bright, Hutchison, and Smith (2) observed the lack of information and measured densities at 25° C. Unfortunately, the compositions studied did not exceed 93.65 per cent SO_3 in H_2O. In addition, the intervals between each density measured were much too large for smooth interpolation.

Electrical conductivity data, on the other hand, were somewhat more extensive than density data, cf. Kohlrausch (5) and Knietsch (4). Gillespie's (3) conductance (and density) work although accurate, was confined to dilute oleums. Walrafen (7), while engaged in Raman intensity studies of oleums, confirmed conductance values of Kohlrausch, Knietsch, and Gillespie (and provided some density data over the full oleum range at 25° C.).

Recently, Raman studies of oleums were repeated by Walrafen (8) and extensive density data (of high accuracy) as well as conductance data were required. To supply the required data the present work was undertaken. Both conductance and density data were obtained as a function of composition for the entire range at 25° C.

EXPERIMENTAL

Stabilized anhydrous sulfur trioxide, (Sulfan B), obtained from the General Chemical Division of Allied Chemical Company, was diluted with fuming sulfuric acid (16-18 wt. % SO_3 in H_2SO_4) to form concentrated oleums. Dilute oleums were made from fuming H_2SO_4 mixed with concentrated H_2SO_4(96-97 wt. %). The compositions desired were prepared by mixing appropriate weighed fractions of the pure colorless reagents. After mixing, the sample was poured into a small vessel equipped with an outside ground glass stopper and partly submerged in a constant temperature water bath at 25 ± 0.01° C.

The determinations of density and composition of oleums were accomplished by first finding the mass-volume relationship followed by titrimetric analysis of the same sample.

A 250λ (0.250 cc.) calibrated micropipette was fitted into an all glass syringe and weighed to 0.1 mg. on an Ainsworth single pan balance which proved to be a valuable aid in measurements requiring speed and precision. Because of the extremely volatile and corrosive properties of oleums, a special acid-resistant lubricant was lightly applied to the plunger of the syringe. The product, Halocarbon Wax (Halocarbon Products), was not completely inert to acids as claimed by the manufacturer, but at high oleum compositions it was superior to others tested.

Without removing the sample bottle from the constant temperature bath, the tip of the pipette was placed into the bottle, the liquid brought slightly above the calibrated mark and removed quickly; traces of excess oleum were wiped from the outside surfaces. The liquid was brought to the mark by deftly touching the end of the pipette with a folded tissue. At high concentrations, the tissues were charred by the acid which caused discoloration of the sample, and cardboard was substituted with better results. The liquid was drawn away from the end of the pipette and a tared glass cap placed over the end. (This procedure avoids weight losses caused by escaping SO_3 vapors). The pipette containing the oleum sample, the protective cap and syringe were weighed together. The density was calculated from the known mass and volume.

To avoid complete dependence on the accuracy of a single pipette, three calibrated pipettes were used interchangeably. Calibrations were carried out by use of distilled water as a reference standard at 25 ± 0.01° C. The mass of the water contained in each pipette was determined to ± 0.05 per cent.

The oleum sample contained in the pipette was transferred quantitatively into a beaker containing a small amount of boiled distilled water. Losses due to volatilization were minimized during sample delivery by keeping the pipette under the water and stirring constantly with a magnetic stirrer. The pipette was rinsed with distilled water from a watch glass. The sample was then titrated with 0.5N sodium hydroxide standardized with potassium acid phthalate (from the Bureau of Standards) and phenophthalein indicator. Four to seven trials were required to achieve mean deviations of <0.05 per cent. In addition, the standard solution was frequently checked and the end point independently determined with a Beckman pH meter. Total weight per cent SO_3 (in H_2O) was determined within 0.05 per cent. Calculation gives $X(SO_3)$, (the stoichiometric mole fraction of SO_3 in a mixture of SO_3 and H_2SO_4).

Electrical conductivities of oleums were measured, (also as a function of composition) at 25 ± 0.01° C. with an Industrial Instruments model RC16B2 conductivity bridge (approximate precision of one per cent). The sample cell used was a Jones-Bollinger type, modified to facilitate sample manipulation. The cell constants were measured with solutions of 0.02N KCl, 0.02N NaCl, and 0.01N HCl. Reliable data pertaining to these solutions are available (6). Sampling and analytical techniques for determining corresponding oleum compositions were essentially the same as those previously described.

RESULTS AND DISCUSSION

Density data are presented in Table I and conductance data appear in Table II. For convenience, the concentrations in both tables are expressed, not only as mole fractions, but also as wt. % SO_3.

Accurate density data are a necessary aid in various studies, e.g., in Raman intensity investigations. The required data can be conveniently interpolated from the smooth curve in Figure 1 which shows density as a function of composition. Starting at 1.825 gram cm. $^{-3}$ for $X(SO_3) = 0$, the curve rises almost linearly, passes through a maximum value—1.995 gram cm. $^{-3}$ for $X(SO_3) \sim 0.65$— and continuously decreases to 1.900 for $X(SO_3) = 1.0$. For the concentration range $X(SO_3) = 0$ to $X(SO_3) \sim 0.7$, the curve is in good agreement with the data of Bright, Hutchison, and Smith. For $X(SO_3) = 1.0$, the extrapolated value is 0.2 per cent lower than that of Berthoud (1). The density

Table I. Densities of Oleums at 25° C.[a]

Wt. % SO_3	Mole Fraction $X(SO_3)$	Density, G./Cc.	Wt. % SO_3	Mole Fraction $X(SO_3)$	Density, G./Cc.
81.77	0.009283	1.8277	89.26	0.4653	1.9631
81.78	0.009946	1.8281	89.58	0.4831	1.9695
82.01	0.02519	1.8325	89.93	0.5024	1.9739
82.04	0.02717	1.8327	90.01	0.5077	1.9752
82.26	0.04165	1.8351	90.41	0.5286	1.9803
82.31	0.04494	1.8363	90.84	0.5519	1.9852
82.39	0.05018	1.8403	91.14	0.5680	1.9904
82.47	0.05541	1.8395	91.33	0.5781	1.9888
82.51	0.05802	1.8425	91.55	0.5898	1.9912
82.65	0.06715	1.8457	91.76	0.6009	1.9920
82.78	0.07559	1.8473	91.82	0.6041	1.9924
82.80	0.07689	1.8464	92.70	0.6501	1.9948
83.01	0.09046	1.8495	92.85	0.6578	1.9952
83.03	0.09175	1.8501	93.30	0.6809	1.9932
83.10	0.09626	1.8535	93.47	0.6895	1.9912
83.44	0.1180	1.8577	93.49	0.6906	1.9908
83.46	0.1193	1.8589	93.51	0.6916	1.9932
83.67	0.1327	1.8647	93.68	0.7002	1.9912
83.75	0.1378	1.8648	93.99	0.7158	1.9888
83.87	0.1454	1.8680	94.06	0.7194	1.9876
83.95	0.1504	1.8677	94.10	0.7214	1.9860
84.14	0.1624	1.8733	94.33	0.7329	1.9844
84.39	0.1770	1.8794	94.70	0.7513	1.9832
84.41	0.1793	1.8804	95.25	0.7784	1.9739
84.54	0.1873	1.8804	95.41	0.7862	1.9763
84.78	0.2022	1.8868	95.81	0.8057	1.9691
84.89	0.2090	1.8870	96.14	0.8216	1.9659
85.17	0.2262	1.8937	96.22	0.8254	1.9639
85.20	0.2281	1.8930	96.55	0.8412	1.9603
85.30	0.2342	1.8954	96.89	0.8574	1.9547
85.45	0.2433	1.8994	96.95	0.8602	1.9525
85.59	0.2518	1.8986	97.26	0.8748	1.9475
85.74	0.2609	1.9022	97.36	0.8795	1.9454
85.90	0.2706	1.9065	97.59	0.8903	1.9418
85.92	0.2718	1.9074	97.90	0.9047	1.9371
86.13	0.2844	1.9098	98.05	0.9116	1.9326
86.37	0.2987	1.9130	98.06	0.9121	1.9350
86.63	0.3142	1.9201	98.07	0.9124	1.9306
86.64	0.3148	1.9189	98.25	0.9208	1.9270
86.81	0.3248	1.9234	98.28	0.9222	1.9282
87.02	0.3372	1.9250	98.66	0.9396	1.9279
87.04	0.3383	1.9275	98.75	0.9438	1.9242
87.25	0.3506	1.9302	98.84	0.9478	1.9182
87.57	0.3692	1.9351	99.02	0.9560	1.9138
87.58	0.3698	1.9347	99.17	0.9628	1.9162
88.03	0.3957	1.9460	99.32	0.9696	1.9134
88.47	0.4209	1.9523	99.57	0.9808	1.9113
88.89	0.4452	1.9599	99.60	0.9822	1.9041
89.05	0.4536	1.9607	99.69	0.9862	1.9070
89.16	0.4597	1.9615	99.71	0.9951	1.9005

[a] Stablized anhydrous liquid sulfur trioxide contains a maximum of 0.25 weight % of stabilizing agent. Therefore, some errors in density, particularly in very concentrated oleums, may result from this source. In regard to this, Berthoud's density data for pure liquid sulfur trioxide (1) (with no stabilizer) are higher than the corresponding data of this work by 0.2%. Presumably, such errors decrease as dilution decreases the concentration of the stabilizer.

Table II. Specific Conductances, κ, of Oleums at 25° C.

| Wt. % SO_3	Mole Fraction $X(SO_3)$	$\kappa \times 10^4$ ohm cm.	Wt. % SO_3	Mole Fraction $X(SO_3)$	$\kappa \times 10^4$ ohm cm.
81.72	0.005956	113	85.23	0.2299	325
81.74	0.007287	119	85.39	0.2397	320
81.80	0.01128	131	85.70	0.2585	308
81.92	0.01923	168	85.75	0.2615	301
81.95	0.02122	150	86.11	0.2832	283
82.00	0.02453	173	86.35	0.2975	266
82.09	0.03047	203	86.79	0.3236	243
82.21	0.03836	221	87.01	0.3366	222
82.28	0.04297	242	87.27	0.3518	199
82.40	0.05083	262	87.54	0.3675	180
82.55	0.06060	283	87.79	0.3818	170
82.61	0.06454	298	88.09	0.3992	136
82.84	0.07948	313	88.34	0.4135	121
83.11	0.09690	331	88.70	0.4339	97
83.43	0.1174	351	88.99	0.4502	82
83.90	0.1472	355	89.32	0.4687	54
84.15	0.1630	351	90.04	0.5084	39
84.35	0.1755	351	90.36	0.5259	26
84.60	0.1911	348	91.17	0.5696	5
84.75	0.2000	348	93.16	0.6737	1
84.76	0.2001	342	100.00	1.0000	~ 0
85.21	0.2287	331			
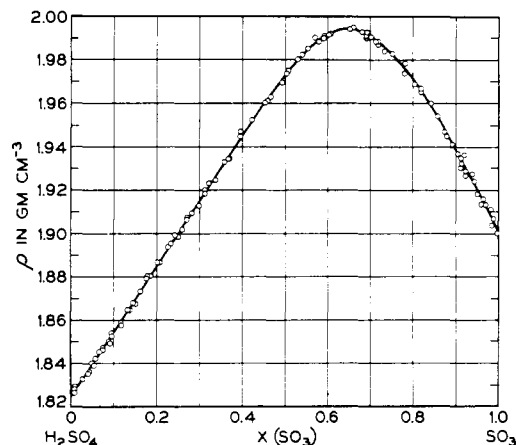
Figure 1. Densities of oleums at 25° C.
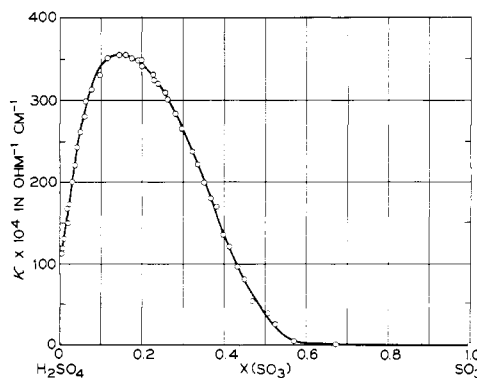
ρ = density, g./cc.

Figure 2. Specific conductances of oleums at 25° C.

κ = specific conductance

data of Knietsch at the higher temperature of 35° C. provide an interesting comparison with the data at 25° C. A qualitative examination shows no significant changes in the thermal expansion from $X(SO_3) = 0$ to $X(SO_3) = 0.45$, but as the concentration increases, changes become more apparent. The largest expansion occurs at $X(SO_3) = 1.0$ and is impressively large.

The conductance measurements presented in Table II and Figure 2 represent the best data available for the concentrations indicated at 25° C.

The curve in Figure 2 rises to a maximum, which constitutes evidence for appreciable ionic dissociation between $X(SO_3) = 0.1$ and $X(SO_3) = 0.2$, then falls off sharply as the concentration is increased.

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Compressibilities of 2-Methyl Pentane and 2,2-Dimethylbutane

RICHARD G. GRISKEY
Virginia Polytechnic Institute, Blacksburg, Va.
and
LAWRENCE N. CANJAR
Carnegie Institute of Technology, Pittsburgh, Pa.

Compressibility data measured for 2-methyl pentane and 2,2-dimethylbutane were limited both as to temperature and density. The present study extends these data to regions not previously investigated.

COMPRESSIBILITIES of 2-methylpentane and 2,2-dimethylbutane in the superheated vapor phase were previously measured by Kelso and Felsing (5) and Felsing and Watson (3), respectively. The 2-methylpentane data comprised two isotherms at 250° and 275° C. and a density range of 1.5 to 5.5 gram mole/liter. Three isotherms (225°, 250°, 275° C.) were determined for 2,2-dimethylbutane for densities from 1.7 to 6.1 grams mole/liter.

The present study was undertaken to extend the temperature and density ranges previously investigated.

The apparatus used to determine the data on the present study was a modification of the design of Keyes (6) and Beattie (1). A detailed description was published by Cherney, Marchman, and York (2), except for certain changes reported by Li and Canjar (7).

An isometric (d = 1.021 gram mole/liter) was measured for 2-methylpentane for temperatures from 230° to 300° C. An additional point at a density of 1.317 gram mole/liter and a temperature of 300° C. was also determined. The 2,2-dimethylbutane data measured in this study consisted of two isometrics (1.092 and 1.378 gram mole/liter). Temperatures for these isometrics varied from 220° C. to 300° C. All experimental data are summarized in Table I.

The data of the present study cannot be directly compared to the data of Kelso and Felsing (5) and Felsing and Watson (3) since the present data are in a density range heretofore not studied.

An indirect comparison was, however, possible by referring to other investigations (4, 5). These studies dealt with compressibilities of n-hexane. One set of data (4) were measured with the apparatus of the present study. The other (5) used the same device as the studies of Kelso and Felsing (5) and Felsing and Watson (3). It was felt that a comparison of these n-hexane data would give some insight as to how the data on the present study compared to existing data.

Figure 1 depicts the n-hexane data. The two sets of data are seen to disagree somewhat at high densities (greater than 3.5–4.5 gram mole/liter). However, the agreement becomes quite good as density decreases. This behavior indicates that the data of the present work should compare favorably to the previously determined data (3, 5).
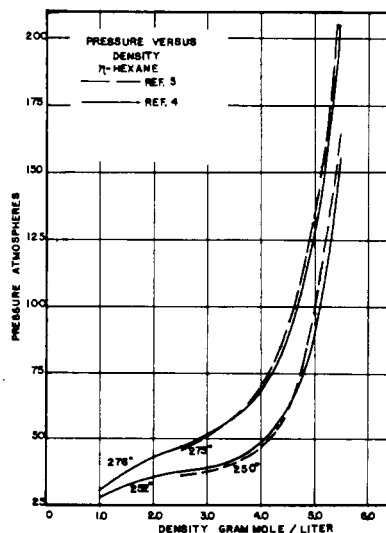

Figure 1. Comparison between data taken with device of present work and that of Felsing and co-workers