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Summary

No difference was found in the atomic weights of specimens of copper from the Calumet and Hecla mines in the Lake Superior region in Michigan and from Chuquicamata, Chile.

The ratio of the atomic weight of copper to that of silver was determined by analysis of pure, recrystallized cupric chloride. The copper was determined electrolytically and the chlorine by nephelometric titration with pure silver. On the basis of Ag = 107.880 the atomic weight of copper was found to be 63.557.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

THE SURFACE TENSION OF LIQUID SULFUR DIOXIDE

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The surface tension of liquid sulfur dioxide has been determined once only and that at a single temperature. At −25° Grunmach[1] found the surface tension of the liquid to be 33.5 dynes per cm. The author has been interested for several years in the work of Dr. Bond[2] of the University of Iowa on solubility. Now Hildebrand[3] recounts the relation between surface tension and solubility. Therefore, it seemed very desirable to determine the surface tension of liquid sulfur dioxide at several temperatures in order that comparisons might be made with other liquids. The problem of the solubility relations of liquid carbon dioxide has already been attacked in this same manner by Quinn.[4]

Experimental

The capillary tube method was used. A large number of capillary tubes were drawn from a variety of soft glass tubes and of these six were chosen for uniformity of bore, determined by means of a micrometer. They were washed with a mixture of potassium dichromate and sulfuric acid for over twenty-four hours. They were thoroughly rinsed with tap water, then with distilled water and finally with conductivity water. They were dried by drawing air through them briefly and were placed in a desiccator over phosphorus pentoxide for more than a week. From the time they were removed from the cleaning solution they were handled with carefully cleaned hands and only at one end. This end was broken off immediately to prevent impurities from

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[1] Grunmach, *Ann. Physik*, [4] **4**, 367 (1901).

[2] Bond and Beach, THIS JOURNAL, **48**, 348–356 (1926); various University of Iowa theses.

[3] Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, **1924**.

[4] Quinn, THIS JOURNAL, **49**, 2704 (1927).

spreading down onto the cleaned portion. The capillaries were loaded into tubes of heavy pyrex glass 1.35 cm. in diameter, sealed at one end. These tubes had been thoroughly cleaned and dried in the same manner as the capillaries. The capillaries were held in a position along the axis of the "jacket" tube by means of two platinum wires bent into a bracket shape, with a loop in the middle. The upper part of the jacket tube was constricted to make subsequent sealing easy.

Liquid sulfur dioxide was prepared by the method mentioned by Bond and Beach[2] except that no mercury seal was used. The apparatus was well swept out by preparing several portions of the liquid. It boiled at −9.8° at 735 mm. pressure, leaving no residue. The jackets were filled about one-fourth full and sealed off at a length of about 10 cm.

A thermostat was constructed of a quart size unsilvered wide-mouthed Dewar flask. This was cooled to −90 and −50° by pouring liquid air into a long test-tube and inserting this tube into the thermostat liquid. Ethyl alcohol was used at the low temperatures. The alcohol would congeal about the tube and furnish a fairly even temperature for some time as it thawed. Ice and calcium chloride were used for the temperature −20°, and salt and ice for −10 and −5°. Ice water and much ice were used for the 0° point. Water at 4° was used to cool tap water to achieve temperatures between 0 and 25°. Temperatures of 30 to 50° were attained by inserting a long narrow lamp commercially used for illuminating showcases. This was turned off and on by means of a home made thermoregulator containing toluene and a mercury contact column. The temperature could easily be controlled within one-tenth of one degree. The light was turned on and off several times per second even when all vibration was eliminated. The bath was stirred efficiently at all temperatures.

The thermometers were checked against one or two standard thermometers recently calibrated by the U. S. Bureau of Standards. At sub-zero temperatures it was necessary to check against freezing and sublimation points. Carbon dioxide, mercury, chloroform, chlorobenzene and carbon tetrachloride were used.

Tubes were kept at the required temperature for thirty minutes to one hour before readings were taken. When working at temperatures somewhat removed from room temperatures, they were placed in a crude cooling bath or warming bath in order that they might come quickly to equilibrium when used.

Readings of the height of the column in the capillary were made by means of a good heavy cathetometer. At least five readings checking within ±0.01 cm. were made. These readings were made with the tube suspended in the thermostat in at least two different positions and at different levels to eliminate errors due to distortion of light by the Dewar flask and the jacket tube. Discrepancies due to this cause were rare. The averages of these readings are recorded in Table II.

After reading the height of the liquid in the capillaries at the various temperatures the tubes were opened. When the sulfur dioxide had completely evaporated, they were rinsed out with some carbon tetrachloride which had been purified by freshly distilling in a tin–glass–air system followed by fractional crystallization. The tubes were now charged with some of the purified carbon tetrachloride, which has a surface tension very close to the value for sulfur dioxide at 20°. The tubes were now suspended in the thermostat and readings were made of the capillary rise. Assuming Richards and Carver's[5] value for the surface tension of carbon tetrachloride to be correct, the radii of the capillaries were calculated

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[5] Richards and Carver, This Journal, **43**, 845 (1921).

from the equation $r = 2\gamma/hdg$, where r is the radius of a capillary, h is the capillary rise corrected as shown below, d is the density of carbon tetrachloride at 20°, g is the acceleration due to gravity and γ is the surface tension of carbon tetrachloride at 20°. The values so found for the radii are listed in Table I.

A second method was employed to determine the radii. A thread of mercury was introduced into each capillary tube and the length of the thread was measured by a micrometer in conjunction with a steel decimeter scale. Incidentally, a check on the uniformity of bore of the capillaries was made by moving the thread along. The length remained practically constant in all cases. The radii were calculated in the obvious manner, after using a microbalance to weigh the mercury by difference. These values are given in the third column of Table I.

The radii were determined finally by breaking the capillaries off squarely and examining them under a microscope fitted with a micrometer. These results are listed in the fourth column of Table I. The mercury method was probably the most exact and these values are used. The fifth and sixth columns give the percentage of deviation from the mercury values. The author did not examine the probable error of these methods. The agreement between the sets was considered very satisfactory.

TABLE I

RADII OF THE CAPILLARY TUBES IN CENTIMETERS

	Method			Deviations	
Tube	1st, CCl_4	2d, Hg	3d, ocular	1st, %	3d, %
1	0.01978	0.01950	0.01995	+1.4	+2.3
2	.01840	.018632	.01868	+1.3	+0.3
3	.00923	.009135	.00923	+1.0	+1.1
4	.01692	.017117	.01736	−1.2	+1.4
5	.02677	.02737	.02729	−0.5	−0.3
6	.01409	.014222	.01430	−0.9	+0.6

Results

The calculations were made in the same manner as those performed by Quinn in the article mentioned. Table II lists the temperature, the tube number, the observed height, the height after two corrections had been made, the densities of the liquid and of the gas, the difference between these values, the surface tension and the average of these numbers at each temperature. The corrections were for volume of the meniscus, and a correction for the effect of the outer tube, made in the same manner as Quinn made them. The densities were read from a large graph upon which had been plotted all the data of densities listed by "International Critical Tables." They were extrapolated mechanically where necessary. Tube No. 3 was thrown out entirely because it was not properly filled with the liquid.

TABLE II

SURFACE TENSION OF SULFUR DIOXIDE

t	Tube	h_1	h_3	D	d	$D - d$	γ	Av. γ
−79	1	2.185	2.258	1.615	0	1.615	(34.07)	
−79	2	2.51	2.589				(38.19)	
−84	4	3.05	3.138				42.53	
−79	5	1.89	1.980				42.91	
−81	6	3.62	3.705				41.72	
−50	1	2.465	2.546	1.5572	0.002	1.555	37.85	
−50	2	2.04	2.106				(29.91)	
−50	4	2.76	2.840				37.06	
−50	5	1.705	1.787				37.29	
−52.3	6	3.300	3.377				36.60	
−20.3	1	2.10	2.170	1.4846	.003	1.482	30.74	
−20	2	2.22	2.291				31.00	
−19.8	4	2.35	2.419				30.08	
−20.2	5	1.48	1.553				30.88	
−20.3	6	2.90	2.969				30.68	30.68
−10	1	1.965	2.031	1.4601	.003	1.457	28.29	
−10	2	2.10	2.167				28.84	
−10	4	2.27	2.337				28.57	
−10	5	1.405	1.474				28.82	
−10	6	2.735	2.800				28.45	28.59
− 5.4	1	1.93	1.995	1.4476	.003	1.445	27.56	
− 5.9	2	2.05	2.116				27.93	
− 5.8	4	2.20	2.265				27.46	
− 6.1	5	1.36	1.428				27.69	
− 5.8	6	2.70	2.765				27.86	27.70
+ 0.2	1	1.86	1.923	1.4350	.004	1.431	26.30	
+ 0.15	2	1.975	2.039				26.65	
+ 0.20	4	2.14	2.203				26.45	
+ 0.30	5	1.34	1.407				27.02	
+ 0.3	6	2.57	2.632				26.87	26.66
+ 5	1	1.82	1.882	1.4223	.004	1.418	25.51	
+ 5	2	1.91	1.972				25.54	
+ 5	4	2.08	2.142				25.49	
+ 5	5	1.30	1.365				25.97	
+ 5	6	2.505	2.566				25.37	25.58
+ 9.9	1	1.76	1.820	1.4095	.0045	1.4050	24.45	
9.9	2	1.87	1.931				24.78	
9.9	4	2.02	2.080				24.52	
9.9	5	1.26	1.323				24.94	
9.9	6	2.445	2.504				24.53	24.54
15	1	1.705	1.763	1.3964	.005	1.3914	23.45	
15	2	1.795	1.853				23.55	
15	4	1.96	2.019				23.58	
15	5	1.225	1.287				24.03	
15	6	2.375	2.433				23.60	23.64
20	1	1.67	1.727	1.3831	.0055	1.3776	22.75	
20	2	1.755	1.812				22.80	
20	4	1.90	1.956				22.61	

TABLE II (*Concluded*)

t	Tube	h_1	h_3	D	d	$D - d$	γ	Av. γ
20	5	1.18	1.240				22.92	
20	6	2.29	2.346				22.54	22.72
24.8	1	1.59	1.655	1.3695	.0060	1.3635	21.57	
24.8	2	1.70	1.756				21.87	
24.9	4	1.84	1.895				21.68	
24.9	5	1.14	1.198				21.42	
24.9	6	2.21	2.264				21.52	21.61
30	1	1.54	1.593	1.3556	.0070	1.3486	20.54	
30	2	1.63	1.684				20.75	
30	4	1.77	1.823				20.63	
30	5	1.105	1.162				21.03	
30	6	2.15	2.203				20.72	20.73
+40	1	1.44	1.490	1.3264	.0100	1.3164	18.75	
40	2	1.515	1.565				18.82	
40	4	1.65	1.70				18.78	
40	5	1.02	1.073				18.95	
40	6	1.975	2.023				18.57	18.77
50	1	1.32	1.366	1.2957	.0144	1.2813	16.73	
50	2	1.395	1.442				16.88	
50	4	1.515	1.561				16.78	
50	5	0.94	0.99				17.02	16.85

Discussion

The equation of de Block mentioned by Quinn was applied to the data between $-20°$ and $+50°$ and found to fit within 0.5%. This equation states that $\gamma = K(t_c - t)^n$, where t is the temperature concerned, in degrees centigrade, t_c is the critical temperature, γ is the surface tension and $K = \gamma_0/(t_c)^n$. Here γ_0 is the surface tension at 0° and n is a constant, equal to 1.2 for most normal unassociated liquids. In the present work n was determined for each experimental datum and the values were averaged, yielding 1.19. However, the median value seemed more desirable on inspection. This value for n is 1.20. The surface tension was therefore

TABLE III

CALCULATED RESULTS

t, °C.	n	$\gamma_{\text{obs.}}$	$\gamma_{\text{calcd.}}$ ($n = 1.2$)	Diff.	$\gamma_{\text{calcd.}}$ ($n = 1.19$)	Diff.
−20	1.17	30.68	30.70	+0.02	30.74	+0.06
−10	1.13	28.59	28.70	+ .11	28.69	+ .10
− 5.8	1.06	27.70	27.84	+ .14	27.83	+ .13
+ 5	1.28	25.58	25.65	+ .07	25.66	+ .08
+ 9.9	1.27	24.54	24.66	+ .12	24.68	+ .14
+15	1.20	23.64	23.64	0	23.67	+ .03
+20	1.20	22.72	22.65	− .07	22.68	− .04
24.5	1.22	21.61	21.69	+ .08	21.73	+ .12
30	1.19	20.73	20.69	− .04	20.73	0
40	1.20	18.77	18.76	− .01	18.81	+ .04
50	1.20	16.85	16.86	+ .01	16.92	+ .07

calculated from both equations, $\gamma = 0.061534(157.5-t)^{1.2}$ and $\gamma = 0.06473(157.5-t)^{1.19}$. The results are entered in Table III, with the deviations of each from the experimental values. The value $n = 1.20$ appears to fit slightly better than $n = 1.19$, although the latter yields smaller maximum deviations. The critical temperature was taken from the work of Cardoso and Fiorentina.[6]

The functions mentioned by Hildebrand,[3] in which E_σ = the total energy of surface formation and v = molal volume, were evaluated as follows: $E_\sigma = 79$ at 20°; $\gamma/\mathrm{v}^{1/3} = 6.33$ at 20°; $E_\sigma/\mathrm{v}^{1/3} = 22$ at 20°. The second function classifies sulfur dioxide between chloroform and benzene in the Hildebrand solubility table.

Numerical values were substituted in the equation of Ramsay and Shields.[7]

$$\frac{\gamma_1\,(M/d_1)^{2/3} - \gamma_2\,(M/d_2)^{2/3}}{t_2 - t_1} = k$$

The data for −20 and +50° place the value of k at 2.134. Non-polar liquids average about 2.12.

This work represents a repetition and an extension of crude experiments reported before the North Dakota Academy of Science on May 4, 1928. The author wishes to express his thanks to Dr. S. C. Lind, Director of the School of Chemistry of the University of Minnesota, for his courtesy in placing facilities of the School at his disposal.

Summary

1. Measurements of the surface tension of liquid sulfur dioxide are reported at temperatures from +50 to −20° with less accurate measurements down to −80° in the undercooled region.

2. The equation of de Block in the form $\gamma = 0.061534(157.5-t)^{1.2}$ is found to fit the experimental data excellently over a 70° range.

3. Several constants depending upon the value of the surface tension are calculated. Results classify liquid sulfur dioxide with benzene and chloroform in its solubility relations.

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[6] Cardoso and Fiorentino, *J. chim. phys.*, **23**, 841 (1926).

[7] Getman, "Outlines of Theoretical Chemistry," John Wiley and Sons, Inc., New York, **1918**, p. 148.