TABLE I

EXPERIMENTAL DATA

Mole $HClO_4$ = mole $Pb(ClO_4)_2$	E_c, mv.	E'
0.1	1.432 ± 3	1.461
.025	1.417 ± 3	1.464
.1	1.407 ± 3	1.466
.0025	1.389 ± 2	1.467
.001	1.378 ± 2	1.467
E_0 by extrapolation of E'		1.467

TABLE II

EXPERIMENTAL DATA

$HClO_4$, mole (per 1000 g. of H_2O)	$Pb(ClO_4)_2$, mole	E_c	E_0
0.25	0.01	1.501	1.475
.25	.001	1.523	1.467
.25	.0001	1.549	1.464
		E_0 average	1.469

Summary

1. The possible sources of error in the previous work on the lead dioxide electrode have been discussed.
2. The work of former investigators who found the first stable value of electrolytically prepared lead dioxide to agree within one or two millivolts with the potential of that obtained from chemical sources has been checked.
3. An attempt has been made to explain the high initial value and the final drop in potential of electrolytic lead dioxide. The factors involved in lengthening the stable period of this lead have also been studied.
4. The effect of lead perchlorate on the hydrogen electrode has been investigated and found to be proportional to the Pb^{++} concentration.
5. The standard oxidation potential of Pb^{++}–PbO_2 in molal H^+ has been measured by two methods and found to be 1.467 ± 0.003 volts.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 205]

SOME OF THE THERMODYNAMIC PROPERTIES OF AMMONIA.

I. THE COMPRESSIBILITY OF AND AN EQUATION OF STATE FOR GASEOUS AMMONIA. THE VAPOR PRESSURE OF LIQUID AMMONIA

BY JAMES A. BEATTIE AND CHARLES K. LAWRENCE

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1. Introduction

The compressibility of gaseous ammonia is of interest because the curvature of the isometries is greater than for any other gas, except steam, for which there is a considerable body of data. The earlier measurements either do not extend over a very wide range, or the volumes were uncertain. Roth[1] studied the pressure–volume–temperature behavior of ammonia from 30 to 180°, but his volumes were not definitely determined;

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[1] Roth, *Wied. Ann.*, 11, 1 (1880).

Brownlee, Babcock and Keyes[2] measured the compressibility for two isotherms, and determined the values of the constants of the Keyes equation of state for ammonia from the existing data, and Keyes[3] presented data for five isometries extending from 39 to 55 cc. per gram and from 60 to 164°. Holst[4] measured the pressure at several volumes and temperatures from 24 to 100° and from 3 to 21 atmospheres; and Bridgman[5] investigated the high pressure field from 1000 to 12,000 atmospheres for the temperature 30°.

Meyers and Jessup[6] of the Bureau of Standards made a study of the compressibility of ammonia in the low pressure region. The measurements were made by the isometric method and extended from 85.5 to 1300 cc. per gram and from -35 to $+300°$. These data will be discussed in a later section.

In the present paper there is presented a series of pressure–volume–temperature measurements on gaseous ammonia, extending from 20 to 95 cc. per gram and from 75 to 325°. These data and those of Meyers and Jessup are correlated by means of an equation of state.

The vapor pressure of liquid ammonia has been measured by Cragoe, Meyers and Taylor[7] of the Bureau of Standards from -80 to $+70°$; and by Keyes and Brownlee[8] from the boiling point to the critical point. The data of the authors, which extend from 30 to 132°, agree very well with those of the Bureau of Standards and fairly well with the values of Keyes and Brownlee.

2. The Experimental Method

All of the measurements were made by the isometric method, the details[9] of which have been described in a paper on the compressibility of gaseous ethyl ether. Some modifications in the apparatus however deserve to be mentioned.

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[2] (a) Brownlee, Babcock and Keyes, *Proceedings of the Third International Congress Refrig.*, Vol. II, p. 189 (1913); also Keyes, *Am. Soc. Refrigerating Eng. J.*, **1**, 9 (1914); (b) Keyes and Brownlee, "The Thermodynamic Properties of Ammonia," John Wiley and Sons, Inc., New York, **1916**, p. 20.

[3] Keyes, *Am. Soc. Refrigerating Eng. J.*, **7**, 371 (1921).

[4] Holst, *Bull. Assoc. International Froid.*, **6**, 48 (1915).

[5] Bridgman, *Proc. Nat. Acad. Sci.*, **9**, 370 (1923).

[6] Meyers and Jessup, *Refrig. Eng.*, 11, 345 (1925). The compressibility of liquid ammonia between saturation and 50 atmospheres is given in Circular of Bureau of Standards, No. **142**, Table 4.

[7] Cragoe, Meyers and Taylor, THIS JOURNAL, **42**, 206 (1920); *Scientific Papers of the Bureau of Standards*, **16**, 1 (1920).

[8] Keyes and Brownlee, THIS JOURNAL, **40**, 25 (1918). See also Keyes, "International Critical Tables," National Research Council, McGraw-Hill Book Co., **1928**, Vol. III, p. 234.

[9] Beattie, THIS JOURNAL, **46**, 342 (1924).

The Thermostat.—A larger thermostat was used in the present investigation. It was a liquid bath 36 cm. in diameter and 75 cm. deep, mineral seal oil being used at the lower temperatures and heavy cylinder oil at the higher temperatures. The stirring was accomplished by three sets of propellers each enclosed in a steel tube and geared together. One of these stirrer casings had a larger tube welded around its lower end, thus forming an annular space about 0.5 cm. in width and 20 cm. long which contained about 200 cc. of mercury. The expansion and contraction of this mercury operated a relay which turned on and off the electric current in the three internal heaters, one of which was placed on the top of each stirrer tube. Sufficient current was constantly passed through external heaters to raise the temperature of the bath to within about 2° of the desired value. The temperature regulation was ±0.001° over the entire range from 75 to 325°.

The temperatures were measured by a four-lead potential type platinum thermometer calibrated as described in the earlier paper. All temperatures are on the platinum scale.

The Pressure Gage.—The gage had been modified somewhat[10] and was calibrated against the vapor pressure of carbon dioxide at 0°, this value being taken as 34.401 atmospheres.[11]

The volume measuring device and piezometer were the same as those used in the measurements on ethyl ether but the connecting and riser block was simplified so that only one steel stopcock was used in the entire volume measuring system.

3. Filling the Piezometer

A commercial sample of liquid ammonia was allowed to stand in a vessel containing sodium for about three months, the gas phase being removed from time to time by "blowing off." The method of filling the glass piezometer was the same as that used for ethyl ether. The ammonia was distilled eight times, the first and last portion being rejected each time, and the ammonia frozen while the entire system was evacuated after each distillation. It was finally distilled into the glass bomb, which had been evacuated for six days, first at 400° and later at 350°. The ammonia was then frozen by liquid air and the bomb sealed. The amount of ammonia used was determined by weighing against a counterpoise which had approximately the same outside and inside volume as the bomb. The counterpoise was evacuated when weighing the loaded bomb so that the buoyancy correction was small.

After each loading the vapor pressure of ammonia was measured at 30°. No increase in vapor pressure was observed even when the gas space was reduced to 0.1 or 0.2 cc. In one case after the gas phase had been completely collapsed, it did not re-form for some minutes even though the external pressure was reduced to less than one atmosphere. After each series of measurements the vapor pressure was determined again but no evidence of a decomposition of the ammonia could be detected.

The method of calculation of the results has been fully described elsewhere.[9] All volumes are relative to those of mercury, whose density at one atmosphere and various temperatures was calculated from the Callendar and Moss equation.[12] The temperature coefficient of the compressibility of mercury used was

$$\frac{1}{V_0}\frac{d}{dp}\left(\frac{dV}{dT}\right) = 5 \times 10^{-9} \text{ atmospheres}^{-1} \text{ degrees centigrade}^{-1}$$

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[10] See Keyes and Dewey, *J. Opt. Soc. Am.*, **14**, 491 (1927).

[11] O. C. Bridgeman, THIS JOURNAL, **49**, 1174 (1927).

[12] Callendar and Moss, *Phil. Trans. Roy. Soc.*, **211**, 1 (1912).

The measured pressures were corrected for the vapor pressure of mercury. For this purpose the saturated vapor pressures of Smith and Menzies[13] were used and a correction applied by the Poynting relation for the effect of pressure on vapor pressure.

Two runs were made: one extending from 95 to 35 cc. per gram, and the other from 40 cc. per gram to higher densities. In this latter run a leak developed at the higher pressures, so that the measurements at densities higher than 20 cc. per gram are too uncertain to include in the data, and the pressures of the 20 cc. per gram isometric may be in error by several tenths of an atmosphere.

4. Discussion of the Experimental Data

The data are given in Table II, in which the measurements of Meyers and Jessup are also included. Since these two sets of results cover different density ranges, they can only be compared by means of some smoothing function, and for this correlation the Beattie–Bridgeman equation of state[14] is used.

The method of determining the values of the constants from the experimental data has been given elsewhere.[14b] In Table I are given the form of the equation of state and the values of the constants in several sets of units. In the evaluation of the constants most weight was given to the authors' data, as they are at the higher densities. The comparison of the observed and calculated pressure is given in Table II, from which it can be seen that the average deviation of the equation from the measured values is 0.037 atmosphere or 0.077% for the author's data, and 0.012 atmosphere or 0.155% for Meyers and Jessup's data.

TABLE I

VALUES OF THE CONSTANTS OF THE BEATTIE–BRIDGEMAN EQUATION OF STATE FOR AMMONIA

$$p = \frac{RT(1-\epsilon)}{V^2}[V+B] - \frac{A}{V^2}$$

$$A = A_0(1 - a/V) \quad B = B_0(1 - b/V) \quad \epsilon = c/VT^3$$

R	A_0	a	B_0	b	c	Mol. wt.
Units: atmospheres; cc. per gram; °C. (T°K. = t°C. + 273.13)						
4.81824	8250	10	2.005	11.222	280×10^6	17.0311
Units: atmospheres; liters per mole; °C.						
0.08206	2.3930	0.17031	0.03415	0.19112	476.87×10^4	17.0311
Units: atmospheres; V = 1 at 0 °C. and 1 atm.; °C. (Amagat units)						
3.71274×10^{-3}	4.8986×10^{-3}	7.706×10^{-3}	1.5451×10^{-3}	8.647×10^{-3}	215.76×10^3	17.0311

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[13] Smith and Menzies, THIS JOURNAL, **32**, 1434 (1910).

[14] Beattie and Bridgeman, (a) *ibid.*, **49**, 1665 (1927); *ibid.*, **50**, 3133 (1928); (b) *Proc. Am. Acad. Arts and Sci.*, **63**, 229 (1928).

TABLE II

COMPARISON OF THE PRESSURES CALCULATED FROM THE EQUATION OF STATE WITH THE OBSERVED PRESSURES

For each temperature the first line gives the observed pressure and the second line gives the observed minus the calculated pressure. The equation used for the calculated pressures is given in Table I.

A. Data of Beattie and Lawrence

Volume, cc./g.		95	90	80	70	60	50	45	40	35	30	25	20
Temp., °C.		Pressures in atmospheres											
325	Obs.	29.59	31.22	35.04	39.90	46.34	55.24	61.11	68.36	77.59	89.69	106.25	130.40
	Obs.−calcd.	−0.07	−0.05	−0.03	−0.03	−0.01	0.00	0.02	0.02	0.05	0.08	0.10	0.12
300	Obs.	28.29	29.84	33.45	38.08	44.18	52.62	58.16	65.03	73.68	85.09	100.61	123.10
	Obs.−calcd.	−0.04	−0.02	−0.03	−0.02	−0.01	0.01	0.01	0.03	0.00	0.05	0.05	−0.02
275	Obs.	26.98	28.44	31.87	36.25	42.00	49.96	55.18	61.62	69.77	80.45	94.88	115.67
	Obs.−calcd.	−0.01	−0.01	−0.01	−0.01	0.02	−0.01	−0.01	−0.01	−0.01	0.04	−0.01	−0.16
250	Obs.	25.64	27.01	30.27	34.39	39.83	47.33	52.22	58.26	65.86	75.74	89.11	108.18
	Obs.−calcd.	−0.01	−0.02	0.00	−0.01	0.00	0.02	0.02	0.03	0.03	0.02	−0.01	−0.21
225	Obs.	24.30	25.59	28.64	32.54	37.64	44.63	49.20	54.81	61.85	70.97	83.21	100.51
	Obs.−calcd.	0.00	−0.01	−0.01	0.01	0.01	0.02	0.02	0.03	0.03	0.02	−0.03	−0.27
200	Obs.	22.93	24.15	27.01	30.64	35.40	41.89	46.12	51.29	57.74	66.05	77.13	92.57
	Obs.−calcd.	−0.02	−0.01	−0.01	−0.01	0.00	0.00	0.01	0.01	−0.01	−0.03	−0.10	−0.39
175	Obs.	21.56	22.70	25.36	28.74	33.14	39.13	43.01	47.73	53.61	61.11	70.98	84.54
	Obs.−calcd.	−0.02	−0.01	−0.01	0.00	0.00	0.01	0.02	0.02	0.03	0.01	−0.06	−0.32
150	Obs.	20.18	21.23	23.70	26.81	30.86	36.33	39.85	44.11	49.36	56.01	64.65	76.24
	Obs.−calcd.	−0.01	−0.01	0.00	0.00	0.02	0.03	0.04	0.05	0.04	0.04	0.00	−0.20
125	Obs.	18.78	19.75	22.00	24.85	28.51	33.44	36.59	40.36	44.99	50.74	58.06	67.56
	Obs.−calcd.	−0.01	0.00	−0.01	0.01	0.01	0.03	0.05	0.05	0.08	0.09	0.08	−0.05
100	Obs.	17.36	18.24	20.28	22.84	26.12	30.47	33.21	36.47	40.41	45.19	51.09	58.28
	Obs.−calcd.	−0.01	0.00	0.00	0.01	0.02	0.03	0.04	0.04	0.07	0.08	0.11	0.04
75	Obs.	15.90	16.68	18.50	20.76	23.61	27.34	29.65	32.35	35.52			
	Obs.−calcd.	−0.01	0.00	−0.01	−0.01	−0.02	−0.02	−0.02	−0.02	−0.02			
50	Obs.	14.37	15.05	16.62	18.54								
	Obs.−calcd.	−0.05	−0.06	−0.07	−0.09								
Av. dev. (atm.)		0.022	0.017	0.016	0.018	0.011	0.016	0.024	0.028	0.034	0.046	0.055	0.178
Av. % dev.		0.101	0.076	0.070	0.073	0.035	0.045	0.059	0.060	0.067	0.076	0.077	0.191

Total average deviation (atm.) 0.037
Total average % deviation 0.077

TABLE II (*Concluded*)

B. Data of Meyers and Jessup

Volume, cc./g.		1300	500	300	200	150	115	85.5
Temp., °C.		Pressures in atmospheres						
300	Obs.			9.126	13.631	18.101	23.497	
	Obs. – calcd.			–0.004	–0.008	–0.010	–0.009	
250	Obs.		5.007	8.308	12.395	16.439	21.305	28.378
	Obs. – calcd.		–0.002	–0.004	–0.007	–0.009	–0.010	–0.018
200	Obs.	1.747	4.519	7.489	11.153	14.766	19.098	25.361
	Obs. – calcd.	–0.001	–0.002	–0.002	–0.005	–0.006	–0.004	–0.007
150	Obs.	1.561	4.030	6.664	9.902	13.075	16.858	22.285
	Obs. – calcd.	0.000	–0.001	–0.003	–0.002	–0.004	–0.001	0.003
100	Obs.	1.374	3.537	5.832	8.632	11.352	14.567	19.109
	Obs. – calcd.	–0.001	–0.002	–0.002	–0.002	–0.004	0.001	0.003
50	Obs.	1.187	3.039	4.985	7.327	9.567	12.162	15.722
	Obs. – calcd.	0.000	–0.003	–0.005	–0.009	–0.017	–0.027	–0.058
35	Obs.						11.391	
	Obs. – calcd.						–0.061	
30	Obs.					8.812	11.129	
	Obs. – calcd.					–0.043	–0.074	
25	Obs.	1.092	2.786	4.549	6.645	8.618		
	Obs. – calcd.	–0.001	–0.005	–0.012	–0.026	–0.052		
15	Obs.				6.361			
	Obs. – calcd.				–0.040			
10	Obs.			4.279				
	Obs. – calcd.			–0.021				
5	Obs.			4.188				
	Obs. – calcd.			–0.024				
0	Obs.	0.997	2.528					
	Obs. – calcd.	–0.001	–0.009					
–10	Obs.		2.421					
	Obs. – calcd.		–0.014					
–20	Obs.	0.921						
	Obs. – calcd.	–0.001						
–30	Obs.	0.882						
	Obs. – calcd.	–0.002						
–35	Obs.	.865						
	Obs. – calcd.	.000						
Av. dev. (atm.)		.001	0.005	0.009	0.012	0.018	0.023	0.018
Av. % dev.		.073	.173	.180	.168	.186	.194	.098
Total average deviation (atm.)					0.012			
Total average % deviation					.155			

The pressures of Meyers and Jessup are all less than those calculated from the equation of state; but it should be noted that in the low pressure region the authors' measured pressures also tend to be less then the calculated values. It is quite evident from the results given in Table II that the general over-all difference between the two sets of data is less than 0.1%. There is, however, a slight difference in the trends of the two sets of measurements which is evident when the A and B functions are plotted against the density. Hence an equation was passed through the Bureau of Standards data alone. The values of the constants and a comparison of the observed and calculated pressures are given in Table III. The average deviation is 0.004 atmosphere or 0.043%. The great difference in the values of the constants for these data may be due either to the fact that the Bureau of Standards measurements are at low pressures where a very slight difference in trend causes a large change in the values of the constants or to the failure of the equation of state to represent the data near saturation within the experimental error, when the constants are determined from measurements at higher temperatures and pressures. It is probable that both of these factors enter into the present case, but it should be emphasized that the authors' data and those of Meyers and Jessup are in excellent agreement, and that the equation of state has reproduced these data very well.

TABLE III

COMPARISON OF THE PRESSURES CALCULATED FROM THE SPECIAL EQUATION OF STATE FOR THE DATA OF MEYERS AND JESSUP WITH THE OBSERVED PRESSURES

The calculated pressures were computed with the values of the constants given below, which were obtained from a consideration of the data of Meyers and Jessup *alone*. The values of the constants (see Table I for the form of the equation) in units of cc. per gram, atmospheres, °C. (T°K. = t°C. + 273.13) are

R	A_0	a	B_0	b	c
4.81824	3000	51.5	0.45	131	360×10^6

The observed pressures are given in Table IIB

Volume, cc./g.	1300	500	300	200	150	115	85.5
Av. dev. (atm.)	0.000	0.001	0.002	0.004	0.005	0.009	0.007
Av. % dev.	.032	.046	.047	.045	.040	.059	.032
Total average deviation (atm.)						0.004	
Total average % deviation						.043	

5. Weight of a Normal Liter of Ammonia

The weight of a liter of a gas at 0° and one atmosphere, usually called the weight of a normal liter, can be calculated from an equation of state and the molecular weight. The weights of a normal liter of several gases[15] have been evaluated by means of the Beattie–Bridgeman equation of state and agree well with the experimental values. By use of the same method the weight of a normal liter of ammonia was computed using the molecular weight 17.0311 and the comparison with the observed values is given in Table IV. The experimental values are those selected by Blanchard and Pickering,[16] who make no attempt to explain the difference between the weight obtained at the Bureau of Standards, which is the result of two different investigators, and those of other careful observers, which

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[15] Beattie and Bridgeman, THIS JOURNAL, **50**, 3151 (1928).

[16] Blanchard and Pickering, *Scientific Papers of the Bureau of Standards*, **21**, 141 (1926).

are all very close to 0.7708. The equation based on the authors' determinations of the compressibility of ammonia leads to the value 0.7706, in good agreement with the earlier data; that based on the data of Meyers and Jessup gives a value of the normal density of 0.7715, agreeing with the Bureau of Standards measured value.

The weight of a normal liter obtained by Keyes[2b] from his equation of state is 0.7699 g.

TABLE IV

WEIGHT OF A NORMAL LITER OF AMMONIA

Source	Grams per liter
Calculated from values of constants of Table I	0.7706
Average of experimental values exclusive of those of Bureau of Standards	.7708
Calculated from value of constants of Table III	.7715
Bureau of Standards experimental value	.7713

6. The Vapor Pressure of Liquid Ammonia

The glass bomb was loaded with about 9 g. of liquid ammonia in the same manner as for a compressibility run. The vapor pressure was measured from 30 to 132°. At each temperature the volume of the vapor space was varied from about 80 cc. to less than 1 cc. Thus at 30° the following values were obtained.

Volume of vapor space (cc.)	76	5	2.4	1.8	0.8	0.2
Vapor pressure (atm.)	11.517	11.514	11.515	11.515	11.516	11.515

These values show that no inert gas was present as there is no increase of the vapor pressure with decrease in volume of the vapor space.

The results are given in Table V, in which are included the measurements made at the Bureau of Standards,[7] and those by Keyes and Brownlee.[8] The agreement with the pressures determined at the Bureau of Standards is better than 0.1%, the authors' pressures being higher, but this difference cannot be explained on the basis of permanent gas in the authors' ammonia since the pressure did not increase with decrease of the vapor volume.

TABLE V

VAPOR PRESSURE OF LIQUID AMMONIA

	Vapor pressure in atmospheres				Vapor pressures in atmospheres	
Temp., °C.	Beattie and Lawrence	Bureau of Standards	Keyes and Brownlee	Temp. °C.	Beattie and Lawrence	Keyes and Brownlee
30	11.515	11.512	....	100	61.779	61.816
40	15.343	15.339	....	110	74.83	74.84
50	20.074	20.059	....	120	89.98	89.80
60	25.815	25.797	....	125	98.45	98.08
70	32.717	32.687	....	130	107.6	106.9
80	40.894	....	40.902	131	109.6	108.8
90	50.526	....	50.558	132	111.5	110.6

7. Summary

The compressibility of gaseous ammonia has been determined from 20 to 95 cc. per gram and from 75 to 325°. These data agree with the

measurements of Meyers and Jessup, which extend from 85.5 to 1300 cc. per gram to better than 0.1%. The constants of the Beattie–Bridgeman equation of state have been determined from these data and their values are given in Table I. The equation of state reproduces the data of the authors with an average deviation of 0.037 atmosphere, or 0.077% and the data of Meyers and Jessup to 0.012 atmosphere or 0.155%.

An equation was passed through the Meyers and Jessup data alone, which represents them to 0.004 atmosphere, or 0.043%.

The weight of a normal liter of ammonia calculated from the equation based on the authors' work is 0.7706 g. and that calculated from the data of Meyers and Jessup is 0.7715 g. The experimental value determined at the Bureau of Standards is 0.7713 g. and the average of all other careful workers is 0.7708 g.

The vapor pressures of ammonia have been determined from 30 to 132°. They agree very well with the Bureau of Standards values, which extend to 70°, and quite well with those of Keyes and Brownlee above 70°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BRITISH COLUMBIA]

THE EFFECT OF TEMPERATURE ON THE MOLECULAR SURFACE ENERGY OF BINARY MIXTURES. I

BY W. F. SEYER AND W. S. PECK

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The surface tension of pure liquids has been a subject of much investigation of late. The molecular surface energy has also received a good deal of attention, though this property has been largely studied from the concentration point of view and little attention has been paid to the effect of temperature on surface energy. It is true that Ramsay and Aston[1] determined the surface tensions of a few binary mixtures over considerable ranges and from the results concluded that in those cases examined the molecular weight of the mixture could be taken as the mean of the values for the two substances, but their work was limited to mixtures somewhat similar in properties. An extensive series of measurements has been carried out by Kremann and Meingast.[2] Unfortunately, the temperature interval over which they measured the surface tension was small and consequently little could be learned from their figures in regard to the effect of temperature on the molecular surface energy of binary mixtures.

An interesting series of solubility relationships is that shown by the

[1] Ramsay and Aston, *Proc. Roy. Soc. London*, **55**, 184 (1894).

[2] Kremann and Meingast, *Monatsh.*, **35**, 1323 (1914).