

to about one-half of one degree. It is difficult to estimate what the corresponding error would be in metallic systems such as the one under consideration, but from preliminary observations in this Laboratory it would appear that the error would be no greater than that just mentioned. The solubility temperature was determined at a number of different rates of heating, 1, 0.25, 0.1° per minute. In Table III the results are for a rate of 0.1° per minute.

From an inspection of Table III it is apparent that these supplementary runs corroborate the data presented in Table II, and thus no maximum in the curve is found for a temperature of 300°. Considerable confidence is placed in these runs using the synthetic method; indeed it appears such a promising method that it is being used in another research in this system in the temperature range 300 to 400°.

### Summary

About fifty determinations of the solubility of gold in mercury have been made, in the temperature interval 200 to 300°, with a modified solubility tube and an air-bath. No maximum in the solubility curve is found, the results being confirmed by six supplementary runs using the synthetic method.

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[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN INVESTIGATIONS,  
BUREAU OF CHEMISTRY AND SOILS]

## THE COMPRESSIBILITY ISOTHERMS OF HELIUM AT TEMPERATURES FROM -70 TO 200° AND AT PRESSURES TO 1000 ATMOSPHERES

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This is the eighth report of a series from this Laboratory concerning the physical properties at high pressures of gases and their mixtures that are of interest in the commercial synthesis of ammonia.<sup>1</sup> It was thought desirable to include helium in this program since its properties would assist in the solution of several problems of importance. The knowledge of the compressibility of a gas which is chemically inactive and only slightly adsorbed by most catalysts will aid greatly in the determination of the adsorption of various gases on catalysts at high pressures. It will also be of value in the theoretical study of gases under high pressures.

The gas was obtained from the Amarillo Helium Plant of the U. S.

<sup>1</sup> (a) Bartlett, *THIS JOURNAL*, **49**, 65 (1927); (b) **49**, 687 (1927); (c) **49**, 1955 (1927); (d) Bartlett, Cupples and Tremearne, *ibid.*, **50**, 1275 (1928); (e) Bartlett, Hetherington, Kvalnes and Tremearne, *ibid.*, **52**, 1363 (1930); (f) **52**, 1374 (1930); (g) Kvalnes and Gaddy, *ibid.*, **53**, 394 (1931).

Bureau of Mines and was 97.8% pure when delivered, the impurities being nitrogen and traces of methane. The crude helium was expanded into a gas-holder through a copper trap filled with charcoal cooled by liquid air. After this operation the analysis indicated an average purity of about 99.5%. The partly purified gas was compressed to about 125 atmospheres, passed under pressure through copper alloy traps containing charcoal kept at liquid air temperature, and finally stored in "200-foot" cylinders until ready for use. The compressibility of the final product did not change when a charcoal trap was put in the line at a point just before the gas entered the high pressure pipet. Refractometric analysis by the Bureau of Standards<sup>2</sup> indicated a purity of 100% with an experimental accuracy of 0.05%. Altogether, nine cubic meters of gas were purified during the course of the experiment.

### Method and Apparatus

The general procedure and the type of apparatus have been described by Bartlett and others.<sup>1b,1d,e,3</sup> The high pressure measurements were made in the following pipets

Pipet	Volume
Chrome vanadium steel pipet <sup>4</sup>	23.081
Chrome vanadium steel pipet	4.095
Copper alloy pipet	3.998

The copper alloy pipet was used principally at the lower temperatures. With the help of Bartlett's values,<sup>1d</sup> the pipets were calibrated at 0° with hydrogen at 100, 200, 500 and 1000 atmospheres. The compressibility factor for helium at 0° and 100 atmospheres based on this calibration was found to be 1.0523 when expressed in Amagat units. (Amagat unit is defined as the ratio of  $PV/P_0V_0$  where  $P$  and  $V$  are the pressure and volume, respectively, at some particular temperature and  $P_0$  and  $V_0$  the corresponding values at 0° and one atmosphere.) The value, 1.0523, was used for checking the volumes of the pipet at frequent intervals. Temperature measurements were made by means of two thermocouples, a five-junction copper-constantan couple for the low-temperature range and a three-junction chromel-X-copel for temperatures above zero degrees centigrade. Both had been calibrated and checked at the Bureau of Standards. The e. m. f. was read on a Leeds and Northrup Type K potentiometer which, including the standard cell, had also been calibrated previously by the Bureau of Standards.

<sup>2</sup> Courtesy of S. F. Pickering, Bureau of Standards.

<sup>3</sup> For a more detailed description of the apparatus see Dilley and Edwards, Dept. of Agriculture, Circular No. 61, 1929.

<sup>4</sup> Composition of chrome vanadium steel: Cr, 1.3%; V, 0.2%; C, 0.2-0.3%. Composition of copper alloy: Cu, 65.00%; Fe, 2.60%; Mn, 5.03%; Zn, 21.69%; Al, 5.72%; Pb, trace.

The old piston and cylinder of the 1000 atmosphere gage<sup>1d</sup> were replaced by new ones. The new piston diameter was 0.48824 cm. and that of the cylinder 0.48870 cm. at the point of equilibrium.

The newly equipped 1000 atmosphere gage was checked against the 200 atmosphere gage<sup>1d</sup> at 200 atmospheres and it was found that the calculated and experimental values checked better than 2 parts in 10,000 at 200 atmospheres. Temperatures were kept constant within 0.05°. The accuracy of calibration of the high pressure pipets is estimated to be 0.03 of 1%. On the average at least three separate runs were made to determine each point. In the majority of cases the maximum deviation between the values obtained in each run was less than 0.05 of 1%; but with the exception of three points at 200° (at 400, 600 and 800 atmospheres), where it was as high as 0.2, the maximum deviation did not exceed 0.1 of 1%. When plotting  $\Delta \equiv V \left( \frac{PV}{RT} - 1 \right)^5$  against temperature it was found that the above three points did not fall on a smooth curve, the first and third were about 0.2 of 1% too low while the second was the same amount too high. With the exceptions mentioned the general accuracy is estimated to be better than 0.1 of 1%. It is hoped at some later date to extend the measurements and determine the three points more accurately.

The experimental results of this investigation are presented in Table I and are expressed in Amagat units. Column 3 gives the direct experimental values; in Column 4 we have calculated the corresponding values from Equations 1-6 which were obtained from the experimental data by the method of least squares, throwing all the adjustment onto the measured volumes.<sup>6</sup> Finally in Columns 5 and 6 the values of Holborn and Otto<sup>7</sup> and Gibby, Tanner and Masson<sup>8</sup> are presented for comparison. The only other work at higher pressures was done by Bridgman,<sup>9</sup> who measured the compressibility of a known weight of 95.8% helium from 3000 to 15,000 kg./sq. cm. The absolute volume at 3000 kg./sq. cm. was unknown and the results given are relative to this unknown volume. He corrected his values for the impurity, assuming it to be nitrogen.

In conclusion the authors take pleasure in acknowledging the friendly coöperation of the staff of the Fixed Nitrogen Research Laboratory; especially we are indebted to Dr. R. T. Milner, who assisted us in the purification of helium.

<sup>5</sup> For this method of plotting consult O. C. Bridgeman, *THIS JOURNAL*, **49**, 1130 (1927).

<sup>6</sup> W. Edwards Deming, *Proc. Phys. Soc. London*, **42**, 97 (1930); *Phil. Mag.*, **11**, January, 1931.

<sup>7</sup> L. Holborn and J. Otto, *Z. Physik*, **33**, 1 (1925).

<sup>8</sup> Gibby, Tanner and Masson, *Proc. Roy. Soc. (London)*, **A122**, 283 (1929).

<sup>9</sup> P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **59**, 173 (1924).

TABLE I

- (1)  $-70^\circ$   $pv = 0.7438 + 0.0005322 p - 0.0000004332 p^2$   
 (2)  $-35^\circ$   $pv = .8721 + 0.0005296 p - .00000004336 p^2$   
 (3)  $0^\circ$   $= 1.00059 + 0.0005217 p - .00000003876 p^2$   
 (4)  $50^\circ$   $pv = 1.18480 + 0.00051043 p - .000000035308 p^2$   
 (5)  $100^\circ$   $pv = 1.3664 + 0.00050442 p - .000000034889 p^2$   
 (6)  $200^\circ$   $pv = 1.73284 + 0.00047795 p - .000000022518 p^2$

Press., atm.	Temp., °C.	$pv$ factors in Amagat units			Gibby, Tanner and Masson <sup>a</sup>
		Experimental	Calculated by Equations 1-6	Holborn and Otto <sup>7</sup>	
100	$-70 \pm 0.05$	0.7964	0.7966	0.7964 <sup>a</sup>	
200		.8490	.8485		
400		.9491	.9498		
600		1.0481	1.0475		
800		1.1417	1.1418		
1000			1.2327		
100	$-50 \pm 0.05$	0.8699		.8696	
100	$-35 \pm .05$	.9249	0.9246	.9245 <sup>a</sup>	
200		.9759	.9763		
400		1.0769	1.0770		
600		1.1744	1.1743		
800		1.2682	1.2680		
900		1.3134	1.3136		
1000			1.3583		
100	0	1.0523	1.0524	1.0522	
200		1.1036	1.1027		
400		1.2026	1.2031		
600		1.3003	1.2996		
800		1.3924	1.3932		
1000		1.4838	1.4835		
100	$50 \pm 0.05$	1.2348	1.2355	1.2346	1.2334
200		1.2859	1.2855		
400		1.3848	1.3833		
600		1.4768	1.4784		
800		1.5706	1.5705		
1000		1.6602	1.6599		
100	$100 \pm 0.10$	1.4162	1.4165	1.4160	1.4141
200		1.4660	1.4659		
400		1.5635	1.5626		
600		1.6553	1.6565		
800		1.7481	1.7476		
1000		1.8359	1.8359		
100	$200 \pm 0.15$	1.7803	1.7804	1.7806	
200		1.8283	1.8275		
400		1.9179	1.9204		
600		2.0152	2.0115		
800		2.0983	2.1008		
1000		2.1889	2.1883		

<sup>a</sup> Interpolated results.

### Summary

The compressibility isotherms of helium have been measured at  $-70$ ,  $-35$ ,  $0$ ,  $50$ ,  $100$  and  $200^{\circ}$  up to  $1000$  atmospheres pressure.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

## THE SYSTEM LITHIUM BROMATE-WATER

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According to A. Potilitzin,<sup>1</sup> crystallization of lithium bromate from aqueous solution results in the formation of a mixture of anhydrous and monohydrate crystals. On the other hand, P. Mylius and R. Funk<sup>2</sup> are of the opinion that the salt exists only in the anhydrous form. This conflict of opinion seemed to justify further investigation concerning the composition of solid phases which are capable of existence when lithium bromate and water are allowed to come to equilibrium at different temperatures.

### Experimental

**Preparation of Lithium Bromate.**—Lithium bromate was made by bringing together solutions of lithium sulfate and barium bromate, titrating one against the other until a drop of either gave no precipitate. The filtrate from the barium sulfate was concentrated and upon cooling lithium bromate crystallized out. Analysis of the dried salt iodimetrically gave in duplicate analyses 99.50 and 100.0% lithium bromate.

### Procedure

All solubility measurements were made by agitating lithium bromate with water in small Pyrex glass-stoppered tubes. Samples of from 0.5 to 1.5 cc. were drawn off by means of pipets into 15-cc. weighing bottles. The solutions were evaporated to dryness and the residues heated to constant weight at  $110^{\circ}$ .

Two sources of error occur in this method of analysis. The salt may suffer some decomposition during drying and there may be a loss of water by evaporation during the transfer of the solution from the solubility tube to the weighing bottle. These errors were shown to be negligible by the following experiments.

(1) 0.5909 g. of lithium bromate was placed in a weighing bottle, water added, then evaporated and the residue heated at  $110^{\circ}$  to constant weight. At the end of this treatment the weight of the residue was 0.5912 g.

(2) Water at  $75^{\circ}$  was transferred to a weighing bottle and allowed to stand exposed to the atmosphere for thirty seconds, during which time

<sup>1</sup> Potilitzin, *J. Russ. Phys.-Chem. Soc.*, **22**, i, 391 (1891).

<sup>2</sup> Mylius and Funk, *Ber.*, **30**, 1718 (1897).