salts which under the conditions produce a precipitate with either ferro- or ferricyanide interfere.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY.]

THE VAPOR PRESSURES OF MERCURY IN THE RANGE 120° TO 250°.

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In a former paper[1] it was pointed out that the values found by various observers for the vapor pressures of mercury are astonishingly discordant. For this and for other reasons there mentioned, the vapor pressures were redetermined at that time over the temperature range 250–435°, using the static isoteniscope.[2] In the present paper a report is made of measurements covering the range 120–250°, using two McLeod gages.

The Existing Data.—The more important observations within the range stated are collected in Table I, in which the observers' names are

TABLE I.

Data of Other Investigators.

Observer.	Temp.	Press. obs. mm. mercury.	Press. calc. from equation R mm. mercury.	Press. diff. Calc. — Obs. mm. mercury.	$\frac{P\text{ calc.}}{P\text{ obs.}} \times 100.$
G	248	71.39	70.29	—1.10	101.6
G	245	68.42	64.89	—3.53	103.0
Y	236.9	51.85	52.03	+0.18	99.6
G	236	51.58	50.72	—0.86	101.7
G	230.5	46.49	43.21	—3.28	107.5
G	224.5	38.82	36.56	—2.26	106.2
G	207	21.07	21.53	+0.46	97.9
H	206.9	22.58	21.47	—1.11	105.2
H	203.0	20.35	18.97	—1.38	107.3
H	190.4	12.89	12.54	—0.35	103.0
G	188	12.51	11.56	—0.95	108.2
H	184.7	11.04	10.32	—0.72	107.0
Y	183.8	9.94	10.00	+0.06	99.4
Y	183.7	9.85	9.97	+0.12	98.8
RY	183.4	9.87	9.87	—0.00	100.0
H	177.4	8.20	7.98	—0.22	102.7
G	176.5	8.22	7.73	—0.49	106.4
H	165.8	5.52	5.22	—0.30	104.3
G	157.5	3.93	3.72	—0.21	105.7
H	154.2	3.49	3.33	—0.16	104.9
G	129	1.00	1.14	—0.14	87.4

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

[2] THIS JOURNAL, 32, 1412 (1910).

abbreviated thus, Young[1] Y, Ramsay and Young[2] RY, Hertz[3] H, Gebhardt[4] G. The "calculated" values are those given by the equation "R" published in 1910,[5] and yield, at least, a smooth curve to serve for purposes of comparison. The amounts of discrepancy are tabulated in the fourth column in mm. of mercury, and, in the fifth column, are made evident by a percentage comparison.

The Method Employed.—The static isoteniscope is not especially well suited for the measurement of the rather low vapor pressures with which we are here concerned, and an entirely new plan was therefore adopted. Two McLeod gages, G and G′ in the diagram (Fig. 1), of suitable capacities were constructed and calibrated. These were connected with each other and with the reservoir A and also, through a mercury seal, with a source of pure dry hydrogen and with a vacuum pump. The gage G′ was completely immersed in an oil bath, fitted with an arrangement for violent stirring,[6] while the gage G and the reservoir A were immersed in water baths at room temperature. By successively admitting and pumping out dry hydrogen, heating the glass meanwhile, the apparatus could be filled with this gas, whose pressure could finally be made whatever was desired prior to closing the mercury seal. If not already done to assist in the removal of adsorbed substances, the gage G′ was raised to the desired temperature, ascertained by a completely immersed mercurial thermometer of known corrections. Both gages were then operated simultaneously, and, because of the condensation on compression of the saturated mercury vapor in G′, gave different readings, from which the required vapor pressure could be calculated. In

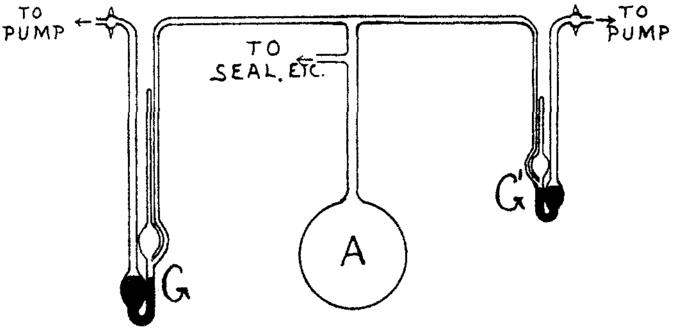

Fig. 1.

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[1] *J. Chem. Soc.*, 59, 629 (1891).

[2] *Ibid.*, 49, 37 (1886).

[3] *Ann. Physik*, [3] 17, 193 (1882).

[4] *Ber. physik. Ges.*, 7, 184 (1905); *Dissertation*, Erlangen, 1903.

[5] *Loc. cit.*

[6] Cf. This Journal, 32, 1421 (1910).

all cases, equilibrium had already become established even at the first reading.

This method is applicable, not only to mercury, but to other substances whose saturated vapors may be suitably introduced into the G′ gage over either mercury, fusible metal or other liquid.

Reduction of Observations.—As identical results for the vapor pressure of mercury were obtained with different pressures of hydrogen, it may be assumed that, in these experiments, the total pressure P in the cold gage is identical with that in the hot gage before the operation of the gages, within the experimental error. Because the gas pressures measured are not negligibly small as compared with the pressure due to the mercury column of the gage, the ordinary formula used for McLeod gages will not apply strictly. Instead, if V is the total volume of the gage, v the volume of the compressed gas trapped in the gage capillary, l the height in mm. of the mercury column chiefly responsible for the compression, and P the pressure in mm. of mercury of the gas in the reservoir A, which it is desired to measure, one may state $P/(l + P) = v/V$; or $P = lv/(V - v)$. This equation was used for the cold gage G, where the vapor pressure of mercury was almost negligible.

In the hot gage G′, the pressure P, prior to the act of compression, is made up of [Hg] the vapor pressure of mercury and $[H_2]$ the partial pressure of hydrogen, whence $[H_2] = P - [Hg]$. After compression, the pressure in the gage capillary is made up of [Hg], as before, plus $[H_2] \times V'/v'$ and this total pressure is also equal to that of the mercury head l' plus P. Thus

$$P + l' = [\mathrm{Hg}] + \{P - [\mathrm{Hg}]\} \times \frac{V'}{v'}$$

or,

$$[\mathrm{Hg}] = P - \frac{v'l'}{V' - v'} = \frac{lv}{V - v} - \frac{l'v'}{V' - v'},$$

which gives the required vapor pressure of mercury.

Precautions to Secure Accuracy.—The hot gage must be sufficiently compact in construction to make possible immersion in the oil bath; but the cold gage may be practically as large as desired. The cold gage reading can thus, ordinarily, be of much higher accuracy. Since the last equation above shows that the hot gage reading is to be subtracted from the cold gage reading to obtain the result, it will obviously be best to arrange to have the hot gage reading relatively rather small, thus reducing its errors to a secondary order. This can be effected by adjusting the hydrogen pressure in the apparatus to have a value not much larger than the anticipated vapor pressure. Again, it should be borne in mind that a McLeod gage reads most accurately for the highest pressures that it will record. The operation of cutting off or trapping the gage gas should be performed very slowly. The readings of heights of mercury columns should, of course, be suitably reduced for temperature and gravitation. A small correction, based on equation "R," was applied to correct for the mercury vapor present in the cold gage.[1]

Measurements Made.—The mercury employed was purified by the customary methods.[2] There was no evidence that it dissolved hydrogen appreciably. In such a case as the present one, all that is necessary is the determination of a very few points. Thermometry in agreement to 0.1° with the 1914 scale of the Reichsanstalt was available only up to 200°, and the 3 points selected are, therefore, below this temperature. The "calculated" values in Table II below are those obtained from the equation

$$\log p = 9.9073436 - 3276.638/\Theta - 0.6519904 \log\Theta \qquad \text{(R)}$$

which was based on measurements between 250° and 435° and published in 1910.[3] The values in the fifth column, which give the percentage change in pressure that would be caused by a temperature change of 0.1°, are also derived from this equation. From the values of the pressure of hydrogen in the reservoir, tabulated under P, one can see that, in these experiments, the accuracy to be expected is greatest at 191.5° and least at 121.8°, for reasons mentioned in a preceding paragraph.

Table II.

Details of Observations

Temperature.	Vapor pressure in mm. mercury at 0°. Found.	Vapor pressure in mm. mercury at 0°. Calc. from R.	$\frac{\text{Found}}{\text{Calc.}} \times 100.$	Percentage change of press. per 0.1° calc from R.	P.
191.5°	13.02	13.02	100	0.34	14.28
150.0°	2.802	2.811	99.67	0.39	3.564
121.8°	0.829	0.823	100.75	0.47	1.738

At 191.5° the agreement between the found and calculated values is only apparently perfect, for the temperature scales concerned differ by several hundredths of a degree at this point.[4] This disagreement between the found and the calculated values, however, is in no case greater than the estimated experimental error.

Conclusions.

The measurements here reported, therefore, indicate that the vapor pressures of mercury between 120° and 250° may be represented, probably to within 1% of their own values, by the same equation "R," without the need of any modification meantime, that was adapted to fit

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[1] It should, perhaps, be mentioned that, at the pressures and compressions used, the divergence of hydrogen from the simple gas law gives rise to errors of an order here quite negligible. Possible systematic error is being further investigated.

[2] Cf. This Journal, **32**, 1439 (1910).

[3] *Ibid.*, **32**, 1441 (1910).

[4] *Ibid.*, **32**, 1440 (1910).

the experimental values formerly found in the range 250° to 435°. The difference between the temperature scales employed in 1910 and in the present work is within the experimental error.

Measurements by this method may be extended to lower temperatures; and the precision here attained may be improved with respect to pressure as well as to temperature. But such further measurements by this method are perhaps unnecessary in view of the greater simplicity of another method, applicable to this and to many other cases, giving results which it is hoped will be published later.

Summary.

(1) A method adapted to the measurement of rather low vapor pressures has been described, involving the use of two McLeod gages, hot and cold, respectively.

(2) This method has been applied to the case of mercury, and it has been shown that the equation connecting pressure and temperature published in 1910 to cover the range 250° to 453° may be applied, without modification of its constants, over the range 120° to 250°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

POTENTIALS OF THE ZINC AND CADMIUM ELECTRODES.

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Normal electrode potential has been defined[1] as the electromotive force of a reversible electrode of the pure element against a solution in which the ion of the element is (hypothetical) molal. This paper presents determinations of the normal electrode potentials of zinc and cadmium referred to the potential of the normal hydrogen electrode as zero.

In a previous, unpublished research[2] a value for the electrode potential of zinc was obtained, based upon measurements of cells containing sulfate solutions as electrolytes. The electromotive force of cells of the type $\underline{Zn}: ZnSO_4: Hg_2SO_4: Hg$ was measured[3] where the zinc sulfate solutions ranged in concentration from 0.005 *M* up to 0.1 *M*. Using the method of calculation employed by Lewis and Lacey[4] to obtain the potential of the copper electrode, and their value of the electromotive force corresponding to the free energy of formation of mercurous sulfate, the value 0.76 volt was obtained as the potential of the zinc electrode. It was

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[1] Lewis, THIS JOURNAL, 35, 22 (1913); 36, 1972 (footnote) (1914).

[2] W. G. Horsch, *Thesis* for the degree of S.M., Univ. of Calif., 1916.

[3]

Molal concn. of $ZnSO_4$ soln.,	0.005	0.010	0.020	0.030	0.070	0.100
Electromotive force,	1.5195	1.5144	1.5054	1.4988	1.4880	1.4830

[4] THIS JOURNAL, 26, 804 (1914).