LXVI. A recalculation of the vapour pressure of mercury

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e is the thermoelectric force of the element copper-platinum for a difference of temperature of 1 degree.

$$e = 0.72 \cdot 10^{-5} \cdot 10^8 \text{ absolute units.}$$

$$e^2 = 0.52 \cdot 10^6,$$

$$\omega' = \frac{273 \cdot 0.52 \cdot 10^6}{2.22 \cdot 4.2 \cdot 10^7} = 15.2 \cdot 10^{-1} \text{ absolute unit,}$$

$$\omega' = 1.52 \cdot 10^{-9} \text{ ohm.}$$

The mean electric conductivity of the alloy is found to be* $3.09 \cdot 10^4$; the specific electric resistance would be

$$\omega = 0.323 \cdot 10^{-4}.$$

Considering the alloy as a single mixture we should find

$$\frac{1}{2}(10.8 + 1.6) \cdot 10^{-6} = 0.062 \cdot 10^{-4}$$

The false resistance is in these cases far too small to explain the difference between the observed and the calculated value of the resistance of the alloys. This result may partly explain why Dr. R. S. Willows† could detect no difference between the apparent resistances of alloys with direct current and with alternating current.

An alloy of equal volumes of copper and iron has a false resistance amounting to 1.5 per cent. of that of copper.

Cambridge, April 6th, 1908.

LXVI. *A Recalculation of the Vapour Pressure of Mercury.*
By T. H. LABY, B.A., *Exhibition of 1851 Research Scholar,*
Joule Student of the Royal Society, Emmanuel College,
Cambridge‡.

THE vapour-pressure of mercury is intrinsically important: it has been determined for a wider range of temperatures than that of any other substance; and Professor Nernst hopes to be able to find the integration constant of the equation of the reaction isochore "by continuing the vapour-pressure curves as far as possible in the direction of very small pressures, for example to .001 mm." § Yet the greatest—and it should be added, unnecessary—disagreement is to be found in the current values of this vapour-pressure, nor is there any table

* *Landolt-Börnstein Physikalisch-chemische Tabellen*, 3 Auflage, p. 721a.

† R. S. Willows, 'Proceedings of the Physical Society of London,' vol. xx. p. 427 (1907).

‡ Communicated by the Author.

§ Nernst, 'Thermodynamics and Chemistry,' New York, 1907, p. 60.

combining all the existing observations. It appeared, then, that a reduction of these numerous observations would be of value.

The existing Data.

The results of the following observers, which are quoted in Table II. after their initial letters, have been obtained by varied methods as indicated below :—

- H.—Hertz (Wied. *Ann.* 1882, xvii. p. 193): Statical method and mercury in glass thermometer corrected by a Joly air-thermometer.
- RY.—Ramsay & Young (Trans. 1886, xlix. p. 37); Young (Trans. 1891, lix. p. 629): Dynamical method, temperatures obtained by vapour-jackets of aniline, quinoline, &c. boiling at known pressures.
- CG.—Callendar & Griffiths (Phil. Trans. 1891, clxxxii. p. 151): Boiling-point of mercury by platinum thermometers in terms of constant-pressure air-thermometer.
- P.—Pfaundler (Wied. *Ann.* 1897, lxiii. p. 36): Absorption (by silver) of mercury from a stream of air saturated with it.
- M.—E. W. Morley (Phil. Mag. [6] vii. p. 662, June 1904): Loss of weight of mercury saturator on passing carbon dioxide through it.
- G.—A. Gebhardt (*Verhand. Deut. Phys. Ges.* 1905, viii. pp. 184–188, and *Diss. Univ. Erlanger*, 1904): Dynamical method, lower pressures measured with a McLeod gauge.
- C.—Cailletet, Colardeau, & Rivièrè (*Compt.-rend.* 1900, cxxx. p. 1585): Static method, thermojunction, and metallic manometer calibrated by open-air manometer.

Few of the observers are explicit as to their unit of pressure, and no mention of the value of g for the place of observation has been found. The latter omission is unimportant as few of the observations are correct to 1 in 1000; but it is more important to know that mm. of mercury means mercury at 0°C .

Regnault's observations have not been used, as he distinctly states they are only approximate, and Ramsay & Young (*loc. cit.*) have given reasons for doubting their accuracy. Nor have I used the results of the elaborate experiments of Van der Plaats*, who was the first to absorb mercury from a stream of gas saturated with mercury vapour, nor those of Hagen† and of McLeod‡, which differ widely from the values deduced from the concordant observations of Hertz, Pfaundler, and Morley. This want of agreement is shown in Table I.

* *Rec. Trav. Chim.* 1886, v. pp. 149–182.

† Wied. *Ann.* 1882, xvi. p. 610.

‡ Brit. Assoc. Rep. 1883, p. 443.

TABLE I.

Temp.	Pressure of Mercury Vapour in mms. according to			
	Van der Plaats.	Hagen.	McLeod.	Hertz, Pfaundler, Morley.
10	·008	—	—	·00042
20	·013	—	·00574	·00109
50	—	·042	—	·0122

In order that the experiments of each observer should contribute about equally to the final result of my reduction, some of the numerically fewer observations of Ramsay & Young, and Young alone have been given 2 †, 3, or 4 times the weight of the other observations, according to the accuracy the writer attached to the measurement of the temperature concerned.

TABLE II.

Observed Vapour-Pressures of Mercury.

	Temp. ° C.	Pressure, in mm.		Temp. ° C.	Pressure, in mm.		Temp. ° C.	Pressure, in mm.
P.	15	·00081	R.Y.	183·4*	9·87	G.	268	122·9
M.	16	·0010	H.	184·7	11·04	R.Y.	270·3	124·35
M.	30	·0027	G.	188	12·51	G.	271·5	126·11
M.	40	·0052	H.	190·4	12·89	G.	277·5	150·8
M.	50	·0113	H.	203	20·35	G.	278·5	147·5
P.	56·3	·01801	H.	206·9	22·58	R.Y.	280·2	157·15
M.	60	·0214	G.	207	21·07	G.	286·5	185·0
M.	70	·0404	R.Y.	222·15	34·4	G.	295·5	224·9
H.	89·4	·16	G.	224·5	38·82	G.	302·5	263·9
P.	98·8	·26305	G.	230·5	46·49	G.	309·5	308·1
H.	117	·71	G.	236	51·58	G.	315·0	360·2
G.	129	1·0	R.Y.	236·95	51·85	CG.	356·7	760
H.	154·2	3·49	G.	245	68·42	C.	400	1596
G.	157·5	3·93	G.	248	71·39	Y.	403·15	2896·9
H.	165·8	5·52	G.	255	87·87	Y.	403·9	2904·5
G.	176·5	8·22	G.	256	94·4	C.	450	3230
H.	177·4	8·2	G.	264	105·69			

* Taking the boiling-point of aniline as 184°·1.

† See Table III., under Δ: this weight is indicated by ×2, &c.

Reduction of Observations.

The logarithms of the observed pressures of the last table were plotted against the temperatures on squared paper 600 by 300 mm., and a ($\log p, t$) curve was drawn through the points. The final curve, or rather formulæ, were then obtained by the following successive approximations.

The most probable values for p at 50° and 250° were found from the above diagram, and a Kirchhoff-Rankine-Dupré formula (B) of the form

$$\log p = A + B/\theta + C \log \theta \quad (\theta = t + 273)$$

was deduced from these values, and the boiling-point $356^\circ\cdot7$. The observed values of t and $\log p$ were replotted (diagram B) on a larger scale, giving a curve about 1100 mm. long when the graph of formula B was drawn in. This figure enabled (as is described below) six points to be found from which a three-constants Kirchhoff formula was calculated by the method of least squares.

The 46 observations from 15° to the boiling-point, at the following temperatures, were arranged thus:—

$$\begin{array}{l} 15^\circ, \quad 16^\circ, \quad 30^\circ, \quad 40^\circ \quad (\text{reduced to } 16^\circ); \\ 50^\circ, \quad 56^\circ\cdot3, \quad 60^\circ, \quad 70^\circ \quad (\text{reduced to } 60^\circ); \\ 89^\circ\cdot4, \quad 98^\circ\cdot8, \quad 117^\circ, \quad 129^\circ \quad (\text{reduced to } 120^\circ); \\ 154^\circ\cdot2, \dots \text{ to } 224^\circ\cdot5 \quad (\text{reduced to } 190^\circ); \\ 230^\circ\cdot5, \quad 236^\circ, \dots \text{ to } 315^\circ \quad (\text{reduced to } 270^\circ); \\ \text{B.P. } 356^\circ\cdot7. \end{array}$$

One value of p was deduced for each group (namely, the values of p at $16^\circ, 60^\circ, 120^\circ, 190^\circ, 270^\circ$) by the process indicated in fig. 1, in which so much of the curve B (one-eighteenth) is drawn as the second group covers. Lines parallel to B were drawn through the observed points $50^\circ, 56^\circ\cdot3, 60^\circ, 70^\circ$ to cut the isotherm 60° in a, b, c, d . The mean position of these four points gave the value of p at 60° . The other groups were similarly treated, and it was found that $\log p$ for the different groups is:—

$$\begin{array}{l} 16^\circ \dots\dots \bar{4}\cdot994 \quad \Bigg| \quad 60^\circ \dots\dots \bar{2}\cdot333 \quad \Bigg| \quad 120^\circ \dots\dots \bar{1}\cdot875 \\ 190^\circ \dots \dots 1\cdot1072 \quad \Bigg| \quad 270^\circ \dots\dots 2\cdot0965 \quad \Bigg| \quad 356^\circ\cdot7 \dots 2\cdot8808 \end{array}$$

But the $\log p = A + B/\theta + C \log \theta$ formula, calculated by the method of least squares from these observations, gave too much weight to the fewer and less accurate low-temperature

observations; and it was clear that one three-constants formula would not fit all the observations as closely as was desirable. The graph of the last formula, however, showed

that two Kirchhoff formulæ could be found, which would fit the observations as closely as was required by the concordance and accuracy of the experiments concerned. These formulæ are :—

$$\log p = 15.24431 - 3623.932/\theta - 2.367233 \log \theta, \quad (M)$$

derived from

$$41.7, \log p = 3.8157; \quad 190^\circ, 1.1072; \quad 270^\circ, 2.0965;$$

$$\text{and } \log p = 10.04087 - 3271.245/\theta - .7020537 \log \theta, \quad (L)$$

derived from

$$16, 4.994; \quad 270^\circ, 2.0965; \quad 356.7, 2.8808.$$

The following Table shows how closely these formulæ fit the observations. M is used from 15° to 270° , and L from 270° to 450° , to calculate $\log p$. Under Δ is given $(\log p \text{ observed}) - (\log p \text{ calculated})$, and under $\Sigma \Delta$ is given the sum of the Δ 's for each group.

TABLE III.

Closeness of fit of formulæ (L and M) to observations.

	t°	Δ	$\Sigma\Delta$		t°	Δ	$\Sigma\Delta$
P.	15	·0687	$-.0247$ $\Sigma\Delta/n$ $= -.0021$	G.	230·5	·0169	$-.0042$ $\Sigma\Delta/n$ $= -.0002$
M.	16	·1213		G.	236	·0046	
M.	30	·0214		G.	245	·0124	
M.	40	·0427		R.Y.	236·95	$-.0137 \times 4$	
M.	50	·0318		G.	248	·0035	
P.	56·3	·0237		G.	255	·0081	
M.	60	·0604		G.	256	·0284	
M.	70	·0713		G.	264	·0092	
H.	89·4	·0180		G.	268	·0140	
P.	98·8	·0075		R.Y.	270·3	$-.0050 \times 2$	
H.	117	·0328		G.	271·5	·0114	
G.	129	·0645		G.	277·5	·0040	
				G.	278·5	·0157	
H.	154·2	·0092	$-.0059$ $\Sigma\Delta/n$ $= -.0004$	R.Y.	280·2	$-.0056 \times 2$	
G.	157·5	·0032		G.	286·5	·0023	
H.	165·8	·0114		G.	295·5	·0008	
G.	176·5	·0127		G.	302·5	·0026	
H.	177·4	·0023		G.	309·5	·0051	
R.Y.	183·4	$-.0142 \times 4$		G.	315·0	·0232	
H.	184·7	·0147					
G.	188·0	·0198		CG.	356·7	·0000	$\Sigma\Delta=0$
H.	190·4	·0027		C.	400	·0083	
H.	203	·0164		Y.	443·9*	·0084	
H.	206·9	·0079		C.	450	·0001	
G.	207	·0236					
R.Y.	222·15	$-.0096 \times 3$					
G.	224·5	·0130					

If the formulæ L and M fitted the observations perfectly, $\Sigma\Delta$ would be zero, while actually $\Sigma\Delta/n$ (where n is the number of observations in each group) has the values $-.0021$, $-.0004$, $-.0002$, and 0. Are these sufficiently small? When it is noticed that the average value of Δ is $.0215$, it will be seen that no real gain is made by decreasing $\Sigma\Delta/n$: the accuracy of the observations does not warrant any efforts to obtain more closely-fitting formulæ.

It is worthy of remark that the formula L, whose constants were determined from p at 16° , 270° , and $356^{\circ}7$, was afterwards found to fit the existing observations to 450° ; and it does not differ from them as much as they differ from one another between 16° and 700° , which shows how well a

* Young's two observations, $443^{\circ}15$ 2896·9 mm. and $443^{\circ}9$ 2904·5 mm., give $443^{\circ}9$ 2916·2 mm. on combining them; this mean is used here.

Kirchhoff formula will express vapour-pressures. Thus, for temperatures above 450° we have :—

Temp.	Formula L.	Cailletet, Colardeau, and Rivière.
450°	3,229 mm.	3,230 mm.
500	6,107 „	6,080 „
550	10,456 „	10,488 „
600	16,943 „	16,948 „
700	38,109 „	38,000 „

TABLE IV.

Vapour-Pressure of Mercury (in mm. of mercury at 0°).

Temp. ° C.	Pressure.	Temp. ° C.	Pressure.	Temp. ° C.	Pressure.	Temp. ° C.	Pressure.
15	·000691	135	1·52	255	86·24	370	959·2
20	·00109	140	1·89	260	97·82	380	1135
25	·00168	145	2·34	265	110·7	390	1337
30	·00257	150	2·88	270	124·8	400	1566
35	·00387	155	3·53	275	140·8	450	3229
40	·00574	160	4·30	280	158·4	Cailletet, Colardeau, & Rivière Observations. Atmospheres.	
45	·00840	165	5·218	285	177·9		
50	·0122	170	6·298	290	199·3		
55	·0174	175	7·567	295	222·8		
60	·0246	180	9·054	300	248·6		
65	·0344	185	10·78	305	276·9		
70	·0476	190	12·80	310	307·7		
75	·0652	195	15·12	315	341·4		
80	·0885	200	17·81	320	378·1		
85	·1191	205	20·89	325	418·0		
90	·1589	210	24·42	330	461·3	500	8
95	·210	215	28·46	335	508·3	550	13·8
100	·276	220	33·03	340	559·1	600	22·3
105	·360	225	38·23	345	614·1	650	34
110	·465	230	44·10	350	673·3	700	50
115	·597	235	50·73	355	737·2	750	72
120	·761	240	58·16	356·7	760 *	800	102
125	·965	245	66·50	360	805·9	850	137·5
130	1·215	250	75·83	365	879·8	880	162

* $\delta p/\delta t$ at the boiling-point = 13·6 mm. per degree.

Extrapolated by formula M :

$$10^{\circ} \cdot 00043, \quad 5^{\circ} \cdot 00026, \quad 0^{\circ} \cdot 00016.$$

Interpolation.

The vapour-pressure may be found for temperatures between those given in the Table by the linear interpolation of

$\log p$ against t ; this is accurate for 5° intervals. Between 365° and 450° , formula L will give p for temperatures not given.

Density and Pressure.

It should be remembered that the vapour-pressure of mercury has not been observed below $89^\circ\cdot4$. Pfaundler and Morley observed the density (for they measured the mass per unit volume) of mercury-vapour in gases saturated with it at different temperatures, and calculated the pressure assuming that the vapour obeys the gas laws and has a density of 100 ($H_2=1$). This is justified at higher temperatures; for Gebhardt, using these assumptions, has calculated the vapour-pressure from the densities of mercury-vapour as observed by Jewett*. The agreement of his results with the actual pressures (see Table V.) is interesting, for it shows that the saturated vapour of mercury is wholly monatomic at nearly half-an-atmosphere pressure.

TABLE V.

Temperature...	140°.	160°.	180°.	200°.	220°.	240°.	260°.	280°.	300°.	310°.
Pressure calc. from density.	1·84	4·23	9·1	24·2	32·2	62·3	100·6	155	250	311 mm.
Pressure from Table IV. ...	1·89	4·30	9·05	17·8	33·0	58·2	97·8	158	249	308 mm.

It does not appear that the critical point of mercury has been reached: it must be at an exceptionally high temperature, apparently above 850° .

LXVII. *Telescopic Vision.*

By G. JOHNSTONE STONEY, *M.A., Sc.D., F.R.S.*†

PART II.—DETERMINATION OF THE KIND OF IMAGE WHICH CAN BE OBTAINED.

[Plate XII.]

CHAPTER 3.

The elementary parts of which an image consists.

32. **I**N the First Part of this Memoir, in the August number of the *Phil. Mag.*, we have described an apparatus (represented in Plate XII., which is reproduced in the present number) with which the astronomer can make experiments that will disclose to him the imperfections

* *Phil. Mag.* [6] vol. iv. 1902, p. 546.

† Communicated by the Author.