LII. Relations between the physical properties of liquids at the boiling-point

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The thermal conductivity was measured by the slab method—a slab of about 300 sq. cm. area and of a thickness of .245 cm. being pressed between a steam and a cold-water vessel. The temperatures of the cold water were read from minute to minute as they rose. Careful corrections were made for “radiation” loss from the cold vessel. Two distinct sets of readings were taken. The values of the conductivity obtained were .000150 and .000141 respectively. Taking the mean of these and employing the value obtained experimentally for the emissivity, viz. .000275, the critical radius becomes .527 cm. The value read off from fig. 3 is about .57. The agreement is as good as was to be expected.

The conclusions to be drawn from these experiments are that :

(1) On narrow steam-pipes, up to about half a cm. external radius, the application of an asbestos coating encourages the escape of heat. This radius is below what may be termed engineering dimensions. But in experimental apparatus it is not at all an unusually small radius ; and for such pipes the application of lagging is a delicate question.

(2) When the radius is much smaller than this critical value, the coat must have an external radius much greater than half a centimetre before the lagging efficiency is as good as without a coat at all. Thus, the curve would seem to show that the escape of heat is the same for external radii of .24 cm. and 2.0 cms.

LII. *Relations between the Physical Properties of Liquids at the Boiling-Point.* By D. TYRER*.

A SIMPLE relation exists between the latent heat of vaporization of a liquid and the molecular volume at the boiling-point. The relation may be expressed

$$LM = K \sqrt[3]{V},$$

where L is the latent heat of a liquid at its boiling-point, V the molecular volume at the boiling-point, M the molecular weight, and K a constant. This relation, which may for the present be regarded as empirical, holds with a fair degree of accuracy for most classes of substances. In the Table given below the values of the molecular volumes are the mean values of the results chiefly of Kopp, Pierre, Schiff, Thorpe, Gartenmeister, and Young. In the last column are given the latent heats calculated according to the above equation, the value of K having been taken as 1583. This figure is the mean value of K for the aliphatic esters, calculated from the results of Schiff and J. C. Brown. As Brown's

* Communicated by Prof. H. B. Dixon, F.R.S.

results are invariably higher than those of Schiff, the agreement between the calculated and observed values of the latent heat will not be so good in those cases where the results of only one of the above observers are known.

Liquid.	Molecular Volume V at the Boiling- Point.	Latent Heat (observed).	Authority.	Mean.	Latent Heat (calculated).
Propyl formate.....	107.0	{ 85.25 90.36	Schiff Brown	87.80	85.41
Isobutyl formate	129.9	{ 77.0 80.12	Schiff Brown	78.56	78.52
Isoamyl formate	151	{ 71.65 73.75 98.26	Schiff Brown Brown	72.70	72.60
Methyl acetate	83.7	{ 97.0	Ramsay & Marshall	97.63	93.57
Ethyl acetate	106.0	{ 83.1 88.37	Schiff Brown	85.73	85.13
Propyl acetate	128.4	{ 77.3 80.45	Schiff Brown	78.87	78.24
Butyl acetate.....	150.6	{ 73.9	Brown	73.9	72.65
Isobutyl acetate	150.1	{ 69.9 72.46	Schiff Brown	71.18	72.47
Isoamyl acetate.....	174	{ 66.35 69.00	Schiff Brown	67.67	67.94
Methyl propionate	104.6	{ 84.15 89.0	Schiff Brown	86.57	84.72
Propyl propionate	150.0	{ 71.5 73.73	Schiff Brown	72.61	72.46
Ethyl propionate	127.8	{ 77.1 80.3	Schiff Brown	78.7	78.72
Isobutyl propionate	174	{ 66.0	Schiff	66.0	67.14
Isoamyl propionate	196	{ 63.05 65.31	Schiff Brown	64.18	63.8
Methyl butyrate	126.7	{ 77.25 79.75	Schiff Brown	78.50	78.07
Ethyl butyrate	150.4	{ 71.5 73.65	Schiff Brown	72.57	72.52
Propyl butyrate	173.9	{ 66.2 68.29	Schiff Brown	67.24	67.98
Propyl isovalerate	192.2	{ 64.37	Brown	64.37	63.91
Isoamyl butyrate	221.5	{ 59.4 61.59	Schiff Brown	60.50	60.58
Isobutyl butyrate	199.2	{ 61.9 64.59	Schiff Brown	63.24	64.16
Methyl isobutyrate	126.5	{ 75.5 79.07	Schiff Brown	77.28	77.9
Ethyl isobutyrate.....	150.7	{ 69.2 71.75	Schiff Brown	70.47	72.56
Propyl isobutyrate	174	{ 63.9	Schiff	63.9	67.94
Isobutyl isobutyrate.....	199.2	{ 59.95 63.4	Schiff Brown	61.67	64.16
Isoamyl isobutyrate.....	223.0	{ 57.65	Schiff	57.65	60.72
Methyl valerate.....	149.1	{ 69.95	Schiff	69.95	72.31
Isoamyl valerate	245.5	{ 56.2	Schiff	56.2	57.25

Liquid.	Molecular Volume V at the Boiling- Point.	Latent Heat (observed),	Authority.	Mean.	Latent Heat (calculated)
Methyl isovalerate	148.7	72.38	Brown	72.38	72.25
Ethyl isovalerate	173.3	67.84	Brown	67.84	67.85
Ethyl caprylate	197.7	60.46	Brown	60.46	63.99
Isobutyl isovalerate	222	60.41	Brown	60.41	60.63
Ethyl nonylate	{ 270 (cal- culated)	58.08	Brown	58.08	56.0
Diethyl carbonate	138.8	72.85	Louginine	72.85	68.85
Chloral	108.9	54.1	Berthelot	54.1	51.10
Chloroform ...	84.5	58.49	Wirtz	58.49	58.09
Carbon tetrachloride	103.7	46.35	Wirtz	46.35	52.34
Ethyl iodide	86.1	{ 46.87 46.0	Andrews Kahlenberg	46.43	44.54
Methylene chloride	65.12	75.3	{ Berthelot & Ogier	75.3	74.87
Ethyl bromide	77.7	{ 60.37 61.65	Wirtz Berthelot	61.01	61.98
Methyl iodide	63.9	46.1	Andrews	46.1	44.54
Acetaldehyde	56.9	136.4	Berthelot	136.4	138.3
Benzene	95.9	{ 94.37 94.93 92.91	Griffiths & Marshall Brown	94.07	92.85
Ethyl benzene ..	138.8	76.4	Wirtz	76.4	77.27
Oymene	184.4	{ 66.3 67.64	Schiff Brown	67.0	67.20
Mesitylene	162.4	{ 71.75 74.42	Schiff Brown	73.08	71.92
Propyl benzene	161.8	71.75	Schiff	71.75	71.83
Terpene	182.8	{ 68.73 68.5 83.55	Favre & Silbermann Schall	68.61	66.01
Toluene	117.9	{ 86.8 87.43	Ramsay & Marshall Brown	85.92	84.34
o-Xylene	138.7	82.47	Brown	82.47	77.25
m-Xylene	139.7	{ 81.34 78.25	Brown Schiff	79.77	77.44
p-Xylene	140.2	80.98	Brown	80.98	77.53
Piperidine	106.3	88.9	Louginine	88.9	88.8
Sulphur oxychloride (SO ₂ Cl ₂)	86.3	52.4	Ogier	52.4	51.79
Tin tetrachloride	131.2	30.33	Andrews	30.33	30.91
Silicon tetrachloride	123.4	37.3	Ogier	37.3	46.3
Carbon disulphide	62.1	83.81	Wirtz	83.81	82.43
Phosphorus trichloride	93.4	51.4	Andrews	51.4	52.4
Ethylene oxide	51.8*	138.6	Berthelot	138.6	134.1
Ethyl propyl ketone	143.3*	82.96	Louginine	82.96	82.78
Dipropyl ketone	165.3*	75.94	Louginine	75.94	76.17
Methyl ethyl ketone	99.3*	103.4	Louginine	103.4	101.7
Pseudocumene	176*	72.8	Schiff	72.8	72.67

* These values of V are calculated from the atomic volumes of Kopp, experimental values not being obtainable.

Properties of Liquids at the Boiling-Point.

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Liquid.	Molecular Volume V at the Boiling- Point.	Latent Heat (observed).	Authority.	Mean.	Latent Heat (calculated).
n. Heptane	162.54	74.0	{ Mabery & Goldstein	74.0	86.33
n. Hexane	139.8	79.4	{ Mabery & Goldstein	79.4	93.3
n. Octane	186.15	{ 70.92 71.1	Louginine Mabery & Goldstein	71.01	79.23
Di-isoamyl.....	231.3	60.85	{ Mabery & Goldstein	60.85	68.35
Ethyl ether	106.1	{ 84.74 90.45	Brown Andrews	87.59	101.3
Amyl ether	246	69.4	{ Favre & Silbermann	69.4	62.77

Liquids whose Molecules Dissociate on Vaporization.

Water	18.78	{ 536.2 535.97 535.9	Berthelot Favre & Silbermann	536.0	233.5
Methyl alcohol.....	42.6	{ 262.2 261.7 263.7	Brown Schall Andrews	262.5	172.7
Ethyl alcohol	62.2	{ 202.4 206.4 205.07	Andrews Schall Wirtz	207.3	136.2
n. Propyl alcohol.....	81.2	{ 216.4 166.3 162.6	Brown Brown Schlamp	164.4	114.1
Formic acid	41.1	{ 120.7 120.37	Favre & Silbermann	120.5	118.7
Acetic acid.....	63.6	{ 84.9 89.79 97.05	Berthelot & Ogier Louginine	90.6	105.2
Butyric acid	108	{ 114.67 113.96	Brown Favre & Silbermann	114.3	85.6
Acetone	77.3	125.3	Wirtz	125.3	116.2
Amyl iodide	150.4	47.5	Berthelot	47.5	42.5
Diethyl oxalate.....	166.2	72.72	Andrews	72.72	59.8
Methyl formate	62.7	{ 116.1 110.45	Andrews & Ogier	113.2	104.7
Ethyl formate	84.7	{ 100.1 100.4	Brown Berthelot & Ogier	100.2	93.9

It will be observed from the Table that there is a close agreement between the calculated and observed values of the latent heat. The only classes of substances which do not seem to conform to the relationship are the aliphatic hydrocarbons and ethers and of course associated liquids as the hydroxyl compounds. The validity of the relation is in general affected by the following factors :—

(1) Experimental errors in the values of the latent heats. These are rather considerable as a comparison of the results of different observers shows. The difference between the calculated and observed values of the latent heat does, as a general rule, come easily within the range of experimental errors except in the few cases mentioned above.

(2) Association of the molecules and their dissociation on vaporization.

The Effect of Molecular Association on the Relation.

The last portion of the above Table deals with liquids which show molecular association, and it will be observed that in these cases there are very wide divergences between the calculated and observed values of the latent heats. The question may be divided into two cases, viz. :—

- (a) Liquids whose molecules are associated but which do not dissociate on vaporization.
- (b) Liquids whose molecules dissociate on vaporization.

Case (a).—In the first case the relation should obviously be written

$$LMn = K \sqrt[3]{Vn},$$

where n is the association factor.

The true latent heat then becomes

$$L = \frac{K \sqrt[3]{V}}{Mn^{\frac{1}{3}}}.$$

Whereas the latent heat L_1 calculated according to the equation without considering association is

$$L_1 = \frac{K \sqrt[3]{V}}{M}.$$

For this class of liquids, therefore, the calculated values of the latent heats will be greater than the observed values.

Case (b).—The second case includes liquids like water, whose molecules are associated in the liquid state, but are normal in the vapour state, and also liquids like amyl iodide,

which on vaporization suffers a partial chemical dissociation into amylene and hydriodic acid.

Suppose that the process of vaporization takes place in two stages, viz.:—(1) The vaporization of the associated molecules without dissociation; (2) the dissociation of the associated molecules of vapour. Let the heat absorbed per associated molecule in the first stage be HMn , where H is the specific heat absorbed, M is the molecular weight, and n is the association factor. This will be equal to $K\sqrt[3]{Vn}$. For the second stage let the heat absorbed per associated molecule be XMn , where X is the specific heat absorbed. Therefore in the complete vaporization of one associated molecule the total heat absorbed (apart from heat required to do external work) may be written

$$HMn + XMn = K\sqrt[3]{Vn} + XMn.$$

And if λ represents the heat required to do external work during the second stage of the vaporization, the true latent heat L_1 of vaporization becomes

$$\begin{aligned} L_1 &= \frac{1}{Mn} \{K\sqrt[3]{Vn} + XMn\} - \lambda, \\ &= \frac{K\sqrt[3]{V}}{Mn^{\frac{2}{3}}} + X - \lambda. \end{aligned}$$

Whereas the calculated latent heat not considering molecular association is

$$L = \frac{K\sqrt[3]{V}}{M}.$$

Therefore we may say that for liquids where molecular dissociation occurs on vaporization, the latent heat calculated according to the equation $LM = 1583\sqrt[3]{V}$ may be either greater or smaller than the observed latent heat according to the magnitude of the heat of dissociation.

It may therefore happen that an associated liquid might not show any deviation from the equation $LM = K\sqrt[3]{V}$. An example is formic acid for which, as it will be noticed from the Table, the calculated value of the latent heat is very close to the observed result. Water and the alcohols give calculated values lower than the observed, whilst some of the acids give higher and some lower calculated values.

On the whole it may be said that with the exception of the aliphatic hydrocarbons and ethers, the relation holds for normal liquids with an exactitude which quite corresponds to the exactitude of the latent heat determinations.

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Indeed, by the aid of the equation $LM = K\sqrt[3]{V}$, the latent heat of a liquid (other than those excepted above) can be calculated merely from a knowledge of its formula with a very fair degree of accuracy. In the above table the values of the molecular volume for several liquids marked with an asterisk are calculated from Kopp's atomic volumes, and it will be noticed that in these cases there is a very fair agreement between the calculated and observed latent heats.

A Relation between the Molecular Volume and the Boiling-Point.

If the relation $LM = K\sqrt[3]{V}$ be combined with Trouton's equation $LM = 20.5 T$ we get a very simple equation

$$T = K_1 \sqrt[3]{V},$$

where T is the temperature of boiling, V is the molecular volume at the boiling-point, and K_1 is a constant.

The value of the constant in Trouton's equation varies for normal liquids from about 19.5 to 22.5. Taking the constant in the equation $LM = K\sqrt[3]{V}$ as equal to 1583 we should expect that the value of K_1 will vary roughly between 70 and 80, and will have a very small value for the aliphatic hydrocarbons and ethers.

The validity of the equation is tested in the following Table. The values of T and V are the mean results of Kopp, Pierre, Buff, Thorpe, Zander, Gartenmeister, Young, and others.

Liquid.	Temperature of Boiling T_{BP} (absolute).	Molecular Volume V at Boiling-Point.	$K_1 = \frac{T_{BP}}{\sqrt[3]{V}}$
<i>Aliphatic Esters.</i>			
Ethyl formate	327.3	84.7	74.53
Methyl acetate	330.1	83.7	75.47
Propyl formate	353.9	107.0	74.54
Ethyl acetate	350.1	106.0	73.98
Methyl propionate	352.7	104.6	74.95
Butyl formate	372	130.7	73.2
Isobutyl formate	370.9	129.9	73.2
Propyl acetate	374.5	128.4	74.2
Ethyl propionate	372	127.8	73.8
Methyl butyrate	375.7	126.7	74.8
n. Amyl formate	403.4	150.5	75.8
Isoamyl formate	396.7	151.0	74.5
Ethyl butyrate	393	150.4	73.9
Methyl valerate	399.3	149.1	75.5
n. Amyl acetate	420.6	173.8	75.4

Liquid.	Temperature of Boiling T_{BP} (absolute).	Molecular Volume V at Boiling-Point.	$K_1 = \frac{T_{BP}}{\sqrt[3]{V}}$.
Isoamyl acetate	409	174	73.2
Ethyl valerate	417.7	174.5	74.8
Isoamyl propionate	433.7	196.0	74.7
Butyl butyrate	438.7	197.8	75.3
Isobutyl butyrate	430.8	199.2	73.7
Propyl valerate	440.5	197.8	75.6
Isopropyl valerate	429	197.2	73.7
Amyl butyrate	457.8	222.3	75.6
Methyl nonylate	477.5	245.7	76.2
Methyl acrylate	353.3	98.4	76.5
Propyl acrylate	395.9	144.9	75.4
Acetaldehyde	294	56.9	76.4
Valeraldehyde	374	119.9	75.8
Paraldehyde	397.4	150.7	74.7
<i>Aromatic Hydrocarbons.</i>			
Benzene	353.2	95.9	77.3
Toluene	382.2	117.9	77.9
o-Xylene	414.7	138.7	80.1
m-Xylene	412	139.7	79.4
p-Xylene	411	140.2	79.2
Ethyl benzene	409.3	138.8	79.1
Cymene	448.3	184.4	78.8
<i>Aliphatic Hydrocarbons.</i>			
n. Hexane	341.9	139.8	65.8
n. Heptane	371.4	161.8	68.2
Diisopropyl	331	136.3	64.3
Diisobutyl	382.2	184.5	67.24
Diisoamyl	432.6	231.3	70.5
Valerylène	314	104	66.8
<i>Aliphatic Ethers.</i>			
Ethyl ether	307.6	106.1	64.9
Methyl propyl ether	311.9	105.1	66.1
Methyl butyl ether	343.3	127.2	63.3
Ethyl propyl ether	336.6	127.8	66.9
Ethyl butyl ether	364	150.1	68.6
Dibutyl ether	413.9	197.3	71.1
<i>Aromatic Esters.</i>			
Methyl benzoate	463	150.3	87.1
Ethyl benzoate	482	174.2	86.3
Methyl phenyl propionate ...	509.6	195.2	87.9
Ethyl phenyl propionate	521.1	221.5	86.3
n. Propyl phenyl propionate..	535.1	245.9	85.4

Liquid.	Temperature of Boiling T_{BP} (absolute).	Molecular Volume V at Boiling-Point.	$K_1 = \frac{T_{BP}}{\sqrt[3]{V}}$
<i>Aromatic Ethers.</i>			
Phenyl propyl ether	463.5	172.0	83.3
Phenyl butyl ether	483.3	195.3	83.3
Phenyl octyl ether	555.8	296.1	83.4
o-Tolyl ethyl ether	457.8	170.9	82.5
o-Tolyl butyl ether	495.0	218.4	82.2
m-Tolyl ethyl ether	465.0	172.0	83.6
m-Tolyl butyl ether	502.2	220.5	83.1
p-Tolyl ethyl ether	462.9	172.1	83.2
p-Tolyl propyl ether	483.4	196.0	83.2
<i>Aliphatic Chlorides.</i>			
Ethyl chloride	285.2	71.2	68.8
Propyl chloride	319.2	91.4	70.9
Isopropyl chloride	309.5	93.6	68.2
Isoamyl chloride	372.6	134.4	72.7
Amyl chloride	374.5	136.3	72.5
Allyl chloride	318.5	84.5	72.6
<i>Aliphatic Bromides.</i>			
Methyl bromide	286	58.2	73.8
Ethyl bromide	312.7	77.7	73.0
Propyl bromide	344	97.2	74.8
Isopropyl bromide	333	97.2	71.9
<i>Aliphatic Iodides.</i>			
Methyl iodide	315.8	84.1	78.1
Ethyl iodide	345.3	86.1	78.2
Propyl iodide	375.5	106.9	79.1
n. Amyl iodide	424.7	150.4	79.9
Butyl iodide	402.9	128.2	79.9
<i>Amines.</i>			
Diethylamine	329	109.1	68.8
Triethylamine	362	153.8	67.6
Tripropylamine	429.5	222.1	70.9
Isobutylamine	340.7	106.2	71.9
Chloroform	334.1	84.5	76.1
Carbon tetrachloride	349.7	103.7	74.3
Ethylene chloride	356.5	85.2	81.0
Ethylidene chloride	331.8	88.7	74.4
Chlorobenzene	405.0	114.3	83.5
Bromobenzene	429.0	119.8	85.0
Iodobenzene	461.4	130.6	90.9
Nitric peroxide N_2O_4	294.6	63.9	73.7
Sulphur dioxide	265	43.9	75.1
Carbon bisulphide	319	62.1	80.6
Tin tetrachloride	387.1	131.2	76.3

<i>Liquids which show Molecular Association.</i>			
Liquid.	Temperature of Boiling T_{BP} (absolute).	Molecular Volume V at Boiling-Point.	$K_1 = \frac{T_{BP}}{\sqrt[3]{V}}$
Water	373	18.78	140.3
Methyl alcohol	337.9	42.6	97.1
Ethyl alcohol	351.3	62.2	88.7
n. Propyl alcohol	370.4	81.2	85.1
n. Hexyl alcohol	429.6	146.3	81.5
Formic acid	373	41.1	108.1
Acetic acid	391.5	63.6	98.0
Propionic acid	413.8	85.5	93.9
Butyric acid	435	108	91.3
Methyl formate	304.7	60.10	76.65
Methyl oxalate	435.6	116.8	89.1
Ethyl oxalate	459.0	166.2	83.5
Propyl oxalate	486.5	215.4	81.2
Dimethyl succinate	468.2	159.7	86.3
Methyl ethyl succinate	481.2	184.6	84.6
Diethyl succinate	489.2	209.6	82.5
Acetonitrile	347	54.3	91.7
Propionitrile	370	78.3	80.1
Valeronitrile	402	119.7	81.6
Phenol	467	103.6	99.4

It will be observed from the Table that the relation gives an approximately constant value of K for all the homologous series, but the value varies considerably from one homologous series to another. In general the higher boiling liquids seem to give rather high values of K . The approximate values of the constant for the different homologous series are given below.

The aliphatic hydrocarbons and ethers give $K=68$.

The aliphatic chlorides and amines give $K=70$.

The aliphatic esters and bromides give $K=74$.

The aliphatic iodides and aromatic hydrocarbons give $K=79$.

The aromatic ethers give $K=83$.

The validity of the relation is also considerably affected by molecular association, as the latter portion of the above Table indicates. For associated liquids the equation should obviously be written

$$T = K\sqrt[3]{Vn},$$

where n is the association factor.

Were it not for the uncertainty of the value of K for

any particular liquid, the above equation would furnish a method of determining n the association factor.

There is one way of distinguishing between the effects of association and constitution. If the members of an homologous series give a gradually diminishing value of K as the series is ascended, then the members of that particular series show molecular association. If the value of K remains approximately constant then no molecular association occurs. For this reason the esters of the aliphatic dibasic acids, like oxalic and succinic, have been classed along with the alcohols and acids as associated liquids.

Mention must be made here of other relations between the molecular volume and the boiling-point. It has long been noticed in a general way that there is a certain parallelism between the molecular volume and the boiling-point, but no exact relation has yet been discovered. Masson (*Phil. Mag.* vol. xxx. p. 412, 1890) discovered empirically the relation $\frac{V}{T} = \text{constant}$, where V and T are the molecular volume and temperature of boiling respectively, which he found to hold closely for the alkyl halides, but apparently only for these few classes of substances.

On the other hand, Young (*Phil. Mag.* vol. xxx. p. 423, 1890) showed that Masson's relation should only hold for substances which have the same critical pressures, and deduced the relation (from van der Waals' generalizations)

$$V = \text{const.} \times \frac{T_c}{P_c},$$

where V is the molecular volume at the boiling-point, T_c is the critical temperature, and P_c the critical pressure. Obviously for those liquids where P_c is constant, Masson's relation will hold.

Summary.

An empirical relation between the latent heat of a liquid and the molecular volume at the boiling-point is shown to hold for most classes of liquids, with the exception of the aliphatic hydrocarbons and ethers and liquids which show molecular association. The relation may be written

$$LM = K \sqrt[3]{V},$$

where L is the latent heat at the boiling-point, M the molecular weight, V the molecular volume at the boiling-point, and K is a constant equal to 1583. The effect of molecular

association on the validity of the relation is examined and it is shown that with associated liquids the calculated value of the latent heat may be either greater or smaller than the actual observed value.

The relation combined with Trouton's equation gives the simple relation

$$T = K \sqrt[3]{V},$$

where T is the boiling-point, V the molecular volume at the boiling-point, and K is a constant. This relation gives a fairly constant value of K for the members of an homologous series, but its value varies rather considerably from one homologous series to another. The relation is also greatly affected by molecular association, the value of K always being much greater for associated liquids than the average.

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LIII. *The Energy Relations of Certain Detectors used in Wireless Telegraphy.* By W. H. ECCLES, D.Sc., A.R.C.S.*

[Plate X.]

THE results of an experimental examination into the physical properties of four very different types of detector used in radio-telegraphy are set forth briefly in the following pages. The conditions of the experiments have been made generally identical with those arising in the ordinary employment of the detectors, and, in particular, the quantities of energy given to the instruments, in the form of electrical oscillations, have been of the same order in these experiments as in actual practice. The detectors investigated are the electrolytic, the carborundum rectifier, the zincite detector, and a thermoelectric detector. All these have before this been subjected to close scrutiny by various observers, who, however, used methods different from that of this paper; a summary of their work will be given alongside the results of the present experiments. These results, it will be seen, are expressed in the form of curves rather than as tables of figures; each curve may be regarded as typical of the detector concerned, and has been selected from a number of curves drawn from measurements accumulated during last year.

The method and apparatus used are the same as were described in a paper "On Coharers," read before the Physical

* Communicated by the Physical Society: read July 8, 1910.