A SPECTROGRAPHIC METHOD FOR THE STUDY OF UNSTABLE COMPOUNDS IN EQUILIBRIUM.

By Ryutaro TSUCHIDA.

Received October 20th, 1934. Published January 28th, 1935.

Introduction. As early as 1921 Professor Y. Shibata established a spectroscopic method for the detection of the formation of complex salts in dilute solution.⁽¹⁾ This method consists in preparing a set of solutions, in which initial concentrations of the components of the molecular compound have simple ratio to each other, and comparing the absorption spectra of these solutions. The ratio of initial concentrations of the components in the solution, which gives the strongest end absorption, shows the ratio of combination of the components to form the molecular compound. Four years later P. Job⁽²⁾ also proposed a similar method.

The present paper deals with a quantitative extension of Prof. Shibata's method in finding composition of unstable compounds and at the same time proposes a general method for the study of chemical equilibrium, determining the equilibrium constant, concentration of unstable compounds, as well as extinction coefficients of the compounds whose spectra are not obtainable without superposition of those of other substances.

The Method. (1) Two substances, A and B, react with each other in dilute solution to form an unstable compound whose composition is unknown.

$$mA + nB \rightleftarrows A_mB_n .$$

$$K = \frac{[A_m B_n]}{[A]^m [B]^n} , \quad \dots\dots\dots\dots\dots\dots\dots \quad (1)$$

where m and n are unknown.

Let the initial concentrations of A and B be a and b respectively, and the concentration of the compound (C) x.

$$K = \frac{x}{(a-mx)^m (b-nx)^n} . \quad \dots\dots\dots\dots\dots \quad (1')$$

Also let the extinction coefficients of A, B and A_mB_n for a wave-length λ_1 be ε_1^A, ε_1^B and ε_1^C respectively, then

---

(1) Y. Shibata, T. Inoue, and Y. Nakatsuka, *J. Chem. Soc. Japan*, **42** (1921), 983; *Japanese J. Chem.*, **1**, (1922), 1; *Chem. Abst.*, **16** (1922), 2075.

(2) P. Job, *Compt. rend.*, **180** (1925), 928; **182** (1926), 1622; *Ann. chim.*, **9** (1928), 143.

$$E_1 = \Sigma\varepsilon c = \varepsilon_1^{\mathrm{A}}(a-mx)+\varepsilon_1^{\mathrm{B}}(b-nx)+\varepsilon_1^{\mathrm{C}}x\,, \quad \ldots\ldots\ldots\ldots \quad (2)$$

where E_1 is measurable absorption of the equilibrium mixture, representing $\Sigma\varepsilon c$ in

$$I = I_0 \times 10^{-\Sigma\varepsilon Cd}\,.$$

Therefore

$$x = \frac{E_1-\varepsilon_1^{\mathrm{A}}a-\varepsilon_1^{\mathrm{B}}b}{\varepsilon_1^{\mathrm{C}}-m\varepsilon_1^{\mathrm{A}}-n\varepsilon_1^{\mathrm{B}}}\,. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

For another wave-length λ_2 and for the same solution,

$$x = \frac{E_2-\varepsilon_2^{\mathrm{A}}a-\varepsilon_2^{\mathrm{B}}b}{\varepsilon_2^{\mathrm{C}}-m\varepsilon_2^{\mathrm{A}}-n\varepsilon_1^{\mathrm{B}}}\,. \quad \ldots\ldots\ldots\ldots\ldots \quad (3')$$

From (3) and (3′)

$$(E_2-\varepsilon_2^{\mathrm{A}}a-\varepsilon_2^{\mathrm{B}}b)\varepsilon_1^{\mathrm{C}}-(E_1-\varepsilon_1^{\mathrm{A}}a-\varepsilon_1^{\mathrm{B}}b)\varepsilon_2^{\mathrm{C}}+\left\{(E_1-\varepsilon_1^{\mathrm{A}}a-\varepsilon_1^{\mathrm{B}}b)\varepsilon_2^{\mathrm{A}}-(E_2-\varepsilon_2^{\mathrm{A}}a-\varepsilon_2^{\mathrm{B}}b)\varepsilon_1^{\mathrm{A}}\right\}m$$
$$+\left\{(E_1-\varepsilon_1^{\mathrm{A}}a-\varepsilon_1^{\mathrm{B}}b)\varepsilon_2^{\mathrm{B}}-(E_2-\varepsilon_2^{\mathrm{A}}a-\varepsilon_2^{\mathrm{B}}b)\varepsilon_1^{\mathrm{B}}\right\}n = 0\,. \quad \ldots\ldots\ldots\ldots \quad (4)$$

As $\varepsilon_1^{\mathrm{A}}$, $\varepsilon_2^{\mathrm{A}}$, $\varepsilon_1^{\mathrm{B}}$ and $\varepsilon_2^{\mathrm{B}}$ may be obtained by measurements of spectra of A and B, all the terms in brackets are known or measurable values and the equation (4) may be expressed as

$$\left.\begin{aligned} & p\varepsilon_1^{\mathrm{C}}-q\varepsilon_2^{\mathrm{C}}+rm+sn = 0\,,\\ \text{where}\quad & p = E_2-\varepsilon_2^{\mathrm{A}}a-\varepsilon_2^{\mathrm{B}}b\,,\\ & q = E_1-\varepsilon_1^{\mathrm{A}}a-\varepsilon_1^{\mathrm{B}}b\,,\\ & r = q\varepsilon_2^{\mathrm{A}}-p\varepsilon_1^{\mathrm{A}}\,,\\ \text{and}\quad & s = q\varepsilon_2^{\mathrm{B}}-p\varepsilon_1^{\mathrm{B}}\,. \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots \quad (4')$$

For various combinations of a and b, the following set of equations are obtained:

$$\left.\begin{aligned} & p_1\varepsilon_1^{\mathrm{C}}-q_1\varepsilon_2^{\mathrm{C}}+r_1m+s_1n = 0\\ & p_2\varepsilon_1^{\mathrm{C}}-q_2\varepsilon_2^{\mathrm{C}}+r_2m+s_2n = 0\\ & \cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\\ & \cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\\ & p_N\varepsilon_1^{\mathrm{C}}-q_N\varepsilon_2^{\mathrm{C}}+r_Nm+s_Nn = 0 \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

By the method of least squares, $\frac{\varepsilon_1^C}{n}$, $\frac{\varepsilon_2^C}{n}$ and $\frac{m}{n}$ may be determined. Being usually small integers, m and n may easily be found from the ratio of m to n, e.g., for $\frac{m}{n} = 0.67$, $m = 2$ and $n = 3$, etc. Consequently ε_1^C and ε_2^C are found. Repeating the above process for various wave-lengths, extinction coefficients and the absorption curve of the unstable compound are obtained.

Substituting these values of ε_1^C, ε_2^C, m, n, etc. in (3), (3′), etc., we can find the concentrations of the compound, from which the equilibrium constant K is calculated.

It is, however, difficult to find the ratio of m to n, if the absorption coefficients of component substances are very small compared with those of the compound. In such cases m and n may conveniently be determined by a spectrographic method similar to the original works of Prof. Y. Shibata.

(2) If both the components, A and B, give no appreciable absorption in spectral regions in which the compound shows absorption, the following method is adopted.

The method consists in preparing a series of mixed solutions, in which initial concentrations of A and B vary to have simple ratio to each other, keeping their sum constant, and measuring the absorption of these solutions. Then the ratio of the initial concentrations of the mixed solution, which gives the highest absorption for the molecular compound, is the ratio of combination, because the maximum concentration for the compound is attained when the ratio of the initial concentrations of the components is exactly the ratio of combination to form the compound. This fact can be proved simply as follows.

From
$$\frac{x}{(a-mx)^m(b-nx)^n} = K\,,$$

and
$$a + b = \text{constant},$$

$$\frac{dx}{da} = \frac{K(a-mx)^{m-1}(b-nx)^{n-1}(mb-na)}{1+K\{m^2(a-mx)^{m-1}(b-nx)^n+n^2(a-mx)^m(b-nx)^{n-1}\}}\,.$$

The condition for the maximum value of x is given by

$$\frac{dx}{da} = 0\,, \quad \text{i.e.} \quad \frac{a}{b} = \frac{m}{n}\,.$$

Prof. Y. Shibata applied this principle only to end absorption in ultraviolet region. It is, however, clear that this principle can be applied to any absorption bands.

(3) If the absorption of one of the components overlaps the absorption of the compound, i.e., the other component only gives no appreciable absorption in spectral parts in which the compound shows absorption bands, it is difficult to find the highest concentration of the compound directly from comparison of a set of absorption curves prepared as in the previous case (2).

Suppose two cases (I and I′) of different initial concentrations, a and a' for A component and b and b' for B component, and let the concentrations of the compound C be x and x' respectively,

$$\frac{x}{(a-mx)^m(b-nx)^n} = \frac{x'}{(a'-mx')^m(b'-nx')^n} .$$

Also let extinction coefficients of B and C at wave-lengths λ_1 and λ_2 be $\varepsilon_1^{\mathrm{B}}$, $\varepsilon_2^{\mathrm{B}}$, $\varepsilon_1^{\mathrm{C}}$ and $\varepsilon_2^{\mathrm{C}}$, the component A giving no appreciable absorption at these wave-lengths. The absorption for these cases (I and I′) is represented in Fig. 1.

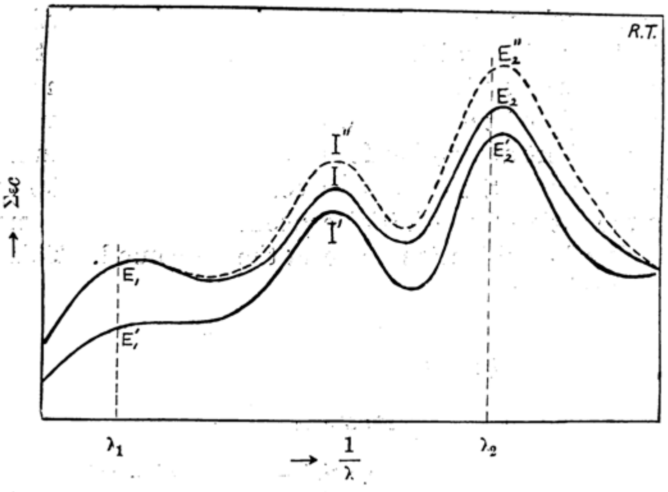

Fig. 1.

At λ_1 and λ_2

$$E_1 = \varepsilon_1^{\mathrm{B}}(b-nx)+\varepsilon_1^{\mathrm{C}}x . \qquad E_2 = \varepsilon_2^{\mathrm{B}}(b-nx)+\varepsilon_2^{\mathrm{C}}x .$$

$$E_1' = \varepsilon_1^{\mathrm{B}}(b'-nx')+\varepsilon_1^{\mathrm{C}}x' . \qquad E_2' = \varepsilon_2^{\mathrm{B}}(b'-nx')+\varepsilon_2^{\mathrm{C}}x' .$$

The difference of $\Sigma\varepsilon c$ at λ_1

$$a_1 = E_1 - E_1' = \varepsilon_1^{\mathrm{B}}\left\{(b-nx)-(b'-nx')\right\}+\varepsilon_1^{\mathrm{C}}(x-x') .$$

The concentration of B corresponding to this absorption difference $\delta = (b-nx)-(b'-nx')+\frac{\varepsilon_1^{\mathrm{C}}}{\varepsilon_1^{\mathrm{B}}}(x-x')$. The absorption which should be given by this quantity of B is added throughout the curve I′. The curve thus drawn is shown as I″ in Fig. 1.

Then the addition to I′ at λ_2

$$\alpha_2 = \varepsilon_2^{\mathrm{B}}\left\{(b-nx)-(b'-nx')\right\}\frac{\varepsilon_1^{\mathrm{C}}\varepsilon_2^{\mathrm{B}}}{\varepsilon_1^{\mathrm{B}}}(x-x') .$$

$$\therefore \qquad E_2'' = E_2'+\alpha_2 = \varepsilon_2^{\mathrm{B}}(b-nx)+\varepsilon_2^{\mathrm{C}}x'+\frac{\varepsilon_1^{\mathrm{C}}\varepsilon_2^{\mathrm{B}}}{\varepsilon_1^{\mathrm{B}}}(x-x') ,$$

therefore

$$E_2''-E_2 = \frac{\varepsilon_1^{\mathrm{B}}\varepsilon_2^{\mathrm{C}}-\varepsilon_1^{\mathrm{C}}\varepsilon_2^{\mathrm{B}}}{\varepsilon_1^{\mathrm{B}}}(x'-x)$$

$$E_2''-E_2 \propto x'-x \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (6)$$

The difference between the curves I and I″ is proportional to the difference of concentrations of C.

This principle affords the means of comparing concentrations of the compound in equilibrium with other substances. Absorption is measured with a series of mixed solutions, in which initial concentrations vary, keeping the sum constant. To the curves of $\Sigma\varepsilon c$, calculated absorption of B is added to make total absorption in all cases the same at one wave-length, and then the heights of the curves at another wave-length are compared. Then the height-differences are proportional to the concentration-differences for the compound in question. The solution corresponding to the highest curve at the wave-length of comparison is of the highest concentration in C and the ratio of the initial concentrations for this solution gives the ratio of combination of A and B to form C. The equalization and comparison may theoretically be executed at any wave-lengths, but, for practical purpose, it is convenient to choose some particular wave-lengths. In order to facilitate the comparison, i.e., to make the difference $E_2''-E_2$ larger, the wave-lengths should be chosen so that the proportionality constant in the relation (6) may attain the highest possible absolute value. This condition may be fulfiled when

1) $\varepsilon_1^{\mathrm{B}}$ and $\varepsilon_2^{\mathrm{C}}$ are as large as possible, and $\varepsilon_1^{\mathrm{C}}$ and $\varepsilon_2^{\mathrm{B}}$ are as small as possible, or 2) vice versa.

In practice, therefore, the wave-lengths of absorption bands are preferably adopted as the points of equalization and comparison. An example of this method is given hereunder.

The Example: The Complex Salt Formation between Potassium Iodide and Iodine. This reaction has been investigated by many authors in various directions, the existence of complex compounds being proved by researches on freezing point depression,(3) solubility,(4) diffusion,(5) conductivity,(6) vapour pressure,(7) adsorption,(8) partition of iodine between two solvents,(9) as well as absorption spectra.(10)

The compositions of these complex compounds are known, but the experiment was carried out as if they were unknown. It is simply because the example is given for the purpose of showing the general procedure of this method.

The equilibrium constant was determined by several authors by measuring vapour pressure,(11) conductivity,(12) partition of iodine in different solvents(13) or solubility.(14)

Of these methods, those which deal with vapour pressure, solubility or partition can be applied only for special cases and are not suitable for general use in studying equilibrium. Compared with these methods, the conductivity method is of more general application, but is apt to suffer a

---

(3) M. Le Blanc and A. A. Noyes, *Z. physik. Chem.*, **6** (1890), 401; E. Paterno and A. Peratoner, *Gazz. chim. ital.*, **21** (1891), 110; S. R. Ray, *J. Ind. Chem. Soc.*, **9** (1932), 268.

(4) A.A. Noyes and J. Seidersticker, *Z. physik. Chem.*, **27** (1899), 360; *J. Am. Chem. Soc.*, **21** (1899), 217; A. P. Laurie, *Pr. Edinb. Soc.*, **29** (1909), 304; *Z. physik. Chem.*, **67** (1909), 627.

(5) G. Edgar and St. H. Diggs, *J. Am. Chem. Soc.*, **38** (1916), 256.

(6) M. Le Blanc and A. A. Noyes, *Z. physik. Chem.*, **6** (1890), 401; P. Lami, *Boll. chim. farm.*, **47** (1908), 435; W. Ridel, Dissert. Halle a.S. 1913; H. Bruns, *Z. Physik*, **34** (1925), 751; E. Thönnessen, *Z. Physik*, **41** (1927), 810; M. Hlasko, *Roczniki chemji*, **6** (1927), 228; W. Birkenstock, *Z. physik. Chem.*, [A], **138** (1928), 432; F. Nies, *Z. physik. Chem.*, [A], **138** (1928), 447.

(7) G. Jones and B. B. Kaplan, *J. Am. Chem. Soc.*, **50** (1928), 1845.

(8) N. Schilow and L. Lepin, *Z. physik. Chem.*, **94** (1920), 57.

(9) A. A. Jakowkin, *Z. physik. Chem.*, **13** (1894), 539; *ibid.*, **20** (1896), 19; H. M. Dawson, *J. Chem. Soc.*, **93** (1908), 1308; R. G. van Name and W. G. Brown, *Am. J. Sc.*, **44** (1917), 106; G. A. Linhart, *J. Am. Chem. Soc.*, **40** (1918), 158; J. N. Pearce and W. G. Eversole, *J. Phys. Chem.*, **28** (1924), 245.

(10) Y. Shibata, T. Inoue, and Y. Nakatsuka, *loc. cit.*; Ch. K. Tinkler, *J. Chem. Soc.*, **91** (1907), 996; *ibid.*, **93** (1908), 1611; P. Job, *Compt. rend.*, **182** (1926), 1622.

(11) G. Jones and B. B. Kaplan, *loc. cit.*

(12) G. Jones and M. L. Hartmann, *J. Am. Chem. Soc.*, **37** (1915), 250.

(13) H. M. Dawson, *J. Chem. Soc.*, **79** (1901), 224; *ibid.*, **81** (1902), 1090; *ibid.*, **93** (1908), 1310; Ch. Winter, *Z. physik. Chem.*, [B], **3** (1929), 303; A. A. Jakowkin, *loc. cit.*; R. G. van Name and W. G. Brown, *loc. cit.*; E. W. Washburn and E. K. Strachan, *J. Am. Chem. Soc.*, **35** (1913), 692; J. N. Pearce and W. G. Eversole, *loc. cit.*; R. Abegg and W. Maitland, *Z. anorg. Chem.*, **49** (1906), 351.

(14) G. Jones and B. B. Kapland, *loc. cit.*; Ch. Winter, *loc. cit.*

great deal from the error caused by the slightest contamination of impurities. On the contrary, the spectrographic method here proposed is more direct than those which consist in measuring partition, vapour pressure, etc. and moreover it is safer than the conductivity method so long as the characteristic absorption bands are the object of the measurement. The spectroscopic method proposed by P. Job,(15) deals only with absorption limit and is not adequate for quantitative calculation of equilibrium constant, etc.

Absorption of mixed solutions of potassium iodide and iodine was photographed with a Spekker photometer and a Hilger spectrograph. Special precaution was taken to avoid photochemical reactions making the time of exposure as short as possible and changing solutions frequently. As the concentration is very small throughout the experiment and total ionization and complete hydration may reasonably be assumed, there is no need of considering change of absorption due to these effects. The absorption of these solutions is shown in Fig. 2 (I, II, III, IV, V and VI) together with the absorption of potassium iodide (A) and iodine (B).

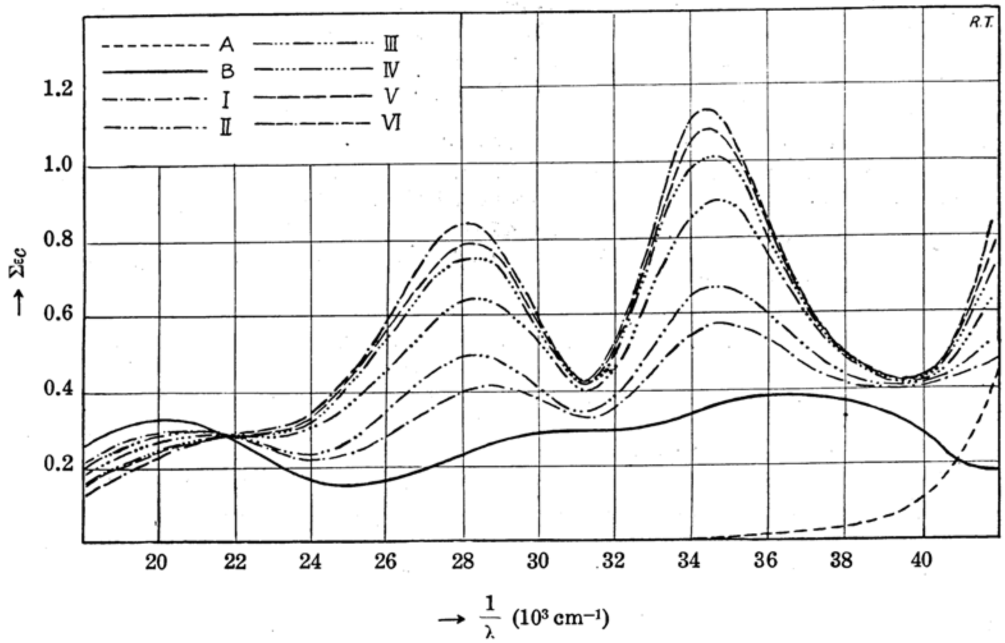

Fig. 2.

---

(15) *Loc. cit.*

The absorption is shown by plotting $\Sigma\varepsilon c$ against wave-number. The initial concentration of potassium iodide a and iodine b, together with E at wave numbers, 20×10^3, 28×10^3, and 34.5×10^3, are given in Table 1.

Table 1. (cf. Fig. 2)

Curve	$a:b$	$a(10^{-5}$mol/l.)	$b(10^{-5}$mol/l.)	d(cm.)	E		
					20×10^3	28×10^3	34.5×10^3
A		100.0	0.0	20			
B		0.0	10.8	1	0.34	0.24	0.36
I	1 : 2	5.0	10.8	1	0.30	0.40	0.57
II	2 : 2	10.0	10.8	1	0.29	0.49	0.67
III	3 : 2	15.0	10.8	1	0.27	0.64	0.89
IV	4 : 2	20.0	10.8	1	0.24	0.75	1.02
V	5 : 2	25.0	10.8	1	0.24	0.79	1.08
VI	6 : 2	30.0	10.8	1	0.22	0.85	1.13

Fig. 2 and Table 1 plainly show that the maximum at 20×10^3 belongs to iodine and the other two maxima at 28×10^3 and 34.5×10^2 to the compound between potassium iodide and iodine. At 22×10^3 all the solutions have the same absorption. It shows that iodine and the compound have the same extinction coefficient at this wave-length. It is also obvious from the curve A that potassium iodide gives no appreciable absorption at the points of absorption maxima of either iodine or the compound. This is exactly the case corresponding to (3) on p. 30.

In order to find m and n empirically, absorption of another series of solutions was measured, varying initial concentrations of potassium iodide and iodine, and at the same time keeping the sum constant. The absorption is shown in Fig. 3.

In Fig. 3 the curves XI, XII, and XIII show the highest absorption in spectral regions of absorption bands of the compound, but it is also clear that these solutions contain more iodine than the rest of the solutions.

E_1 at wave number 20×10^3 is measured. The differences of E_1's are shown in Table 3 as α_1 and δ is the corresponding quantity of iodine. α_2 shows the addition at wave number 34.5×10^3. Then E_2 at the same wave number plus α_2 gives E_2''.

Fig. 4 shows the curves after the graphical addition. Differences of these curves are theoretically proportional to the differences of concentrations of the molecular compound as we have shown above in the relation (6). We can, therefore, plainly see from these curves that the molar ratio of

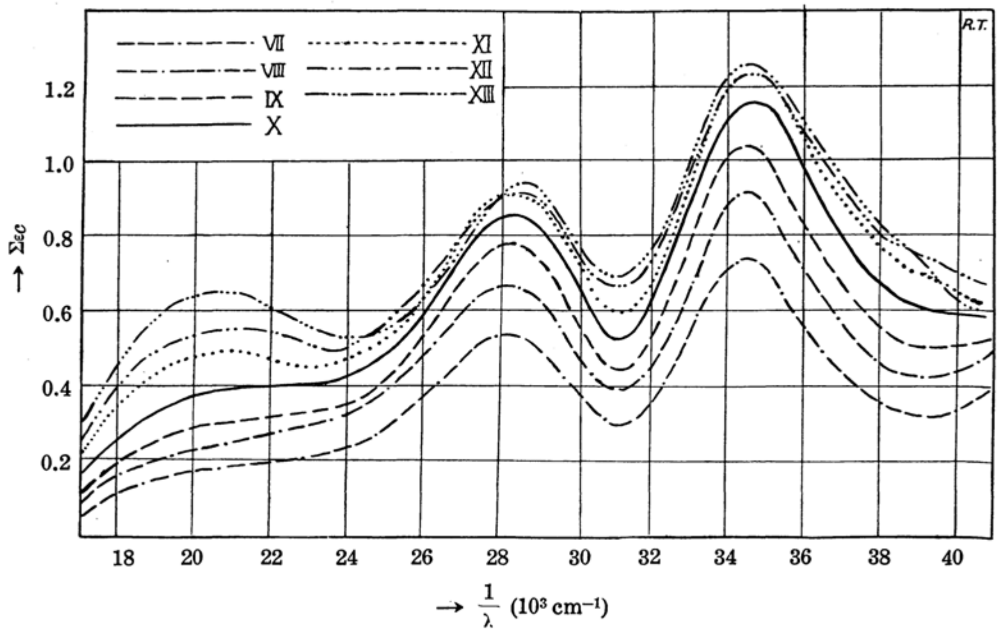

Fig. 3.

Table 2. (cf. Fig. 3)

Curve	$a:b$	a(10^{-5}mol/l.)	b(10^{-5}mol/l.)	d(cm.)	E		
					20×10^3	28×10^3	34.5×10^3
VII	3 : 1	22.5	7.5	1	0.18	0.54	0.74
VIII	2 : 1	20.0	10.0	1	0.22	0.66	0.90
IX	3 : 2	18.0	12.0	1	0.29	0.77	1.04
X	1 : 1	15.0	15.0	1	0.37	0.84	1.14
XI	2 : 3	12.0	18.0	1	0.48	0.90	1.23
XII	1 : 2	10.0	20.0	1	0.55	0.90	1.23
XIII	1 : 3	7.5	22.5	1	0.64	0.91	1.25

Table 3. (Fig. 3 and Fig. 4)

Curve	E_1	E_2	α_1	δ(10^{-5}mol/l.)	α_2	E_2''
	20×10^3	34.5×10^3				
VII	0.18	0.74	0.46	14.6	0.47	1.21
VIII	0.22	0.90	0.42	13.3	0.43	1.33
IX	0.29	1.04	0.35	11.1	0.36	1.40
X	0.37	1.14	0.27	8.6	0.28	1.42
XI	0.48	1.23	0.16	5.1	0.16	1.39
XII	0.55	1.23	0.09	2.9	0.09	1.33
XIII	0.64	1.25	0.00	0.0	0.00	1.25

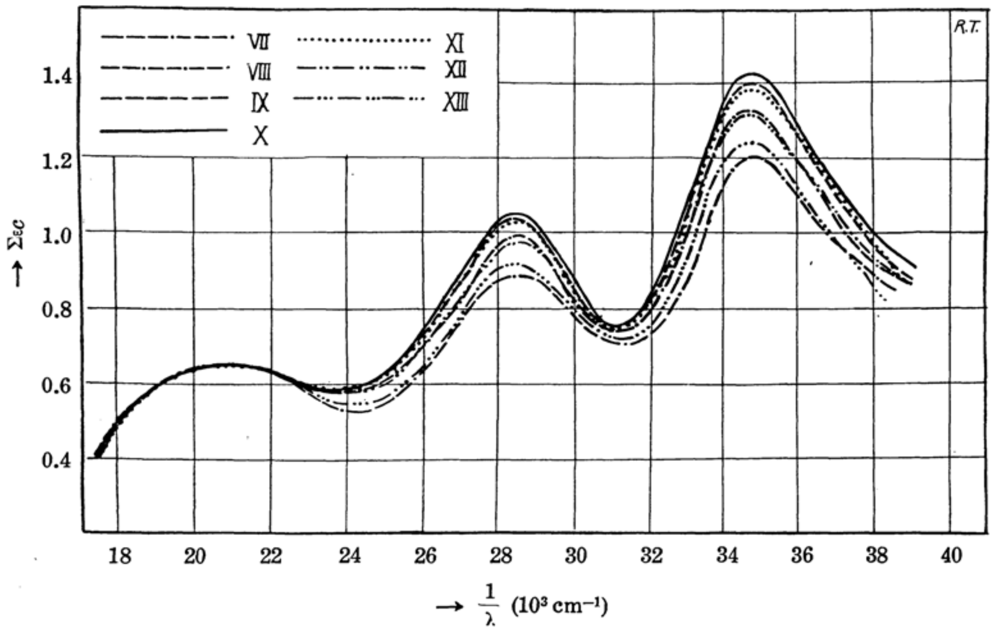

Fig. 4.

combination between potassium iodide and iodine, in our case, is one to one, as the curve X gives the highest absorption at wave numbers 28×10^3 and 34.5×10^3, which correspond to the absorption bands of the molecular compound. Thus m and n are found to be 1 and 1, the formula for the molecular compound being, therefore, KI_3.

We can calculate extinction coefficients for the compound KI_3, substituting m, n and experimental spectrographic data as below in the equations (1′), (3) and (3′).

$m = 1$ $\varepsilon_1^B = 0.22 \times 10^4$ extinction coeff. of iodine at 28×10^3
$n = 1$ $\varepsilon_2^B = 0.32 \times 10^4$,, ,, ,, at 34.5×10^3

The extinction coefficients of the potassium triiodide at wave numbers 28×10^3 and 34.5×10^3 were found to be 1.20×10^4 and 1.58×10^4 respectively.

Substituting these values in the equations (3) and (3′),

$$\text{i.e.,} \quad x = \frac{p}{15800-3200} \quad \text{and} \quad x = \frac{q}{12000-2200},$$

concentrations of potassium triiodide in each case in Fig. 2 and Fig. 3 were calculated. These values of x are shown in Table 4 together with the equilibrium constant calculated for them.

Table 4.

Curve	a (10^{-5}mol/l.)	b (10^{-5}mol/l.)	E_1	E_2	p	q	$\frac{p}{12600}$	$\frac{q}{9800}$	x (10^{-5}mol/l.)	K (10^3)
I	5.0	10 8	0.40	0.57	0.22	0.16	1.8	1.6	1.7	5.7
II	10.0	10.8	0.49	0.67	0.32	0.25	2.6	2.7	2.7	4.6
III	15.0	10.8	0.64	0.89	0.54	0.40	4.3	4.1	4.2	5.9
IV	20.0	10.8	0.75	1.02	0.67	0.51	5.3	5.2	5.3	6.5
V	25.0	10·8	0.79	1.08	0.73	0.55	5.7	5.6	5.7	5.8
VI	30.0	10.8	0.85	1.13	0.78	0.61	6.3	6.2	6.3	5.6
VII	22.5	7.5	0.54	0.74	0.50	0.37	4.0	3.8	3.9	5.8
VIII	20.0	10,0	0.66	0.90	0.58	0.44	4.6	4.5	4.6	5.5
IX	18.0	12.0	0.77	1.04	0.63	0.50	5.0	5.1	5.1	5.7
X	15.0	15.0	0.84	1.14	0.65	0.52	5.1	5.3	5.2	5.4
XI	12.0	18.0	0.90	1.23	0.63	0.50	5.0	5.0	5.0	5.5
XII	10.0	20.0	0.90	1.23	0.57	0.45	4.5	4.5	4.5	5.3
XIII	7.5	22.5	0.91	1.25	0.52	0.41	4.1	4.3	4.3	6.7

The mean value of the equilibrium constant between 23° to 25° is 5.6×10^3. The deviation in the equilibrium constant is supposed to be caused by the flactuation of temperature, as the experiment was carried out at room temperature.

Subtracting the calculated absorption of iodine and potassium iodide from the curve VI which has the mean value of K, the absorption for potassium triiodide is worked out. (Fig. 5)

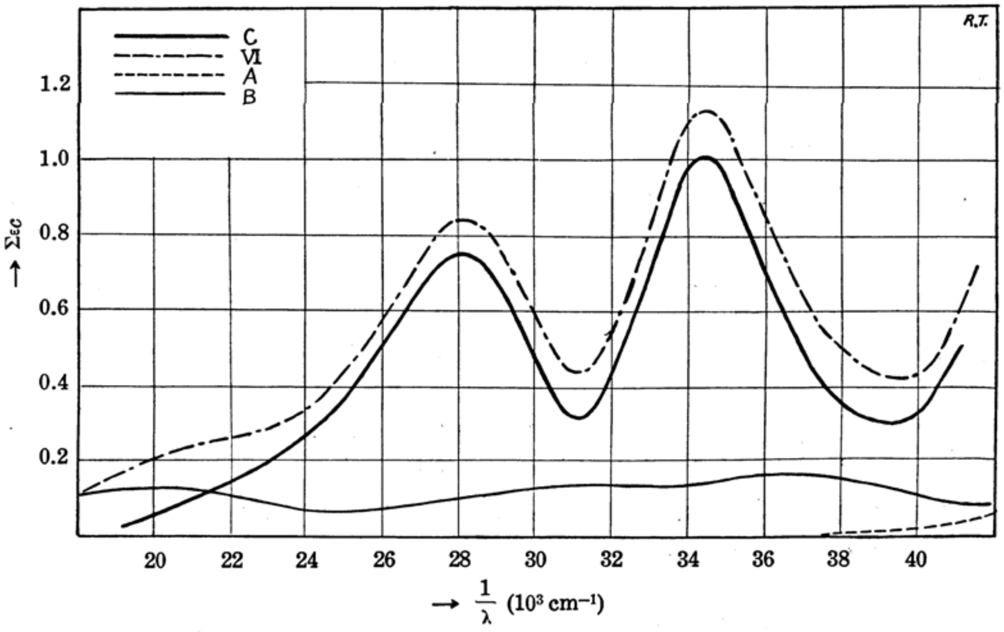

Fig. 5.

The absorption has two maxima at 360 mμ and 290 mμ and minima at 320 mμ and 250 mμ. The extinction coefficients at the maxima are 1.20×10^4 and 1.58×10^4.

An experimental evidence for the relation (6) is given in Fig. 6 in which E_2'' in Table 3 is plotted against x in Table 4.

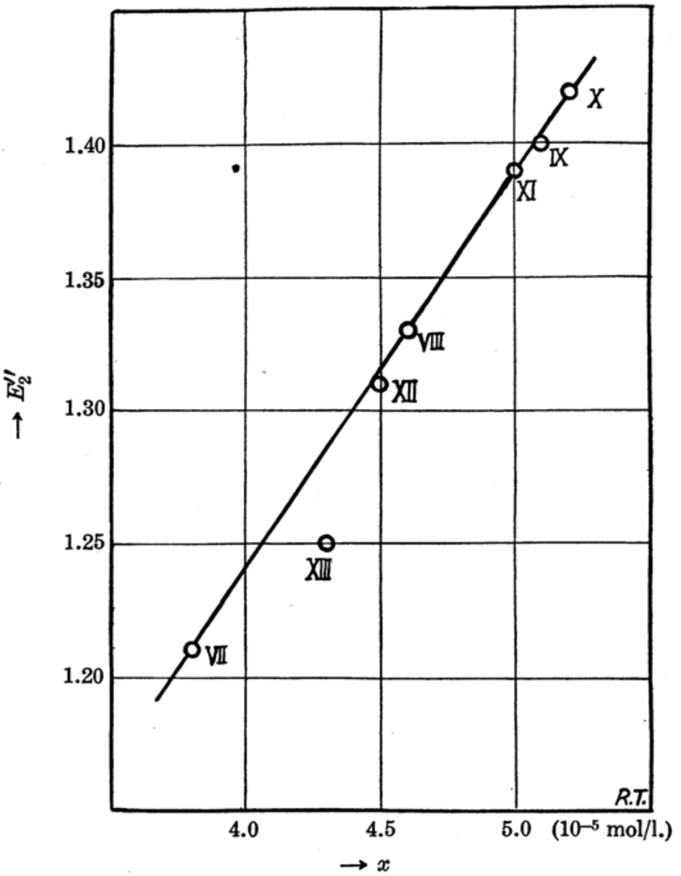

Fig. 6.

Fig. 6 shows that E_2'' is a linear function of x, i.e., the difference of E_2'' is proportional to the difference of concentrations of the compound. The tangent of this line is 15×10^3, and the calculated value of $\frac{\varepsilon_1^B\varepsilon_2^C-\varepsilon_1^C\varepsilon_2^B}{\varepsilon_1^B}$ is 14.8×10^3. ($\frac{\varepsilon_2^B}{\varepsilon_1^B}=1.1$ from Fig. 2, $\varepsilon_2^C=15.8\times10^3$ as given above and $\varepsilon_1^C=\frac{0.06}{6.3\times10^{-5}}=0.95\times10^3$ from Fig. 5 and Table 4.)

As it is clear from the calculation, the relation (6) holds not only for absorption, but also for other physical properties, such as refraction, optical rotation, etc. We may, therefore, take various combinations of physical properties, e.g., absorption at λ_1 and optical rotation at λ_2. This method can be applied not only to the study of molecular compounds as in this example but also can be widely applied to general study of chemical reactions in liquid and in gaseous state.

The examples for these applications will follow.

The author wishes to express his thanks to Prof. Y. Shibata and Mr. C. F. Goodeve for their kind interest in this work.

The Sir William Ramsay Laboratory,
University College, London.