NOTE ON THE SOLUBILITY OF SOLID NON-ELECTROLYTES

By R. Negishi

One of the most useful equations expressing the properties of regular solutions is that derived by Hildebrand and Wood[1] by making use of the probability function of Menke[2] as a basis for a statistical treatment[3] of intermolecular potentials in solution. It is :

$$\bar{E}_2 - E_2^0 = \left(\frac{n_1 V_1}{n_1 V_1 + n_2 V_2} \right)^2 V_2 \left[\left(\frac{\varDelta E_2}{V_2} \right)^{\frac{1}{2}} - \left(\frac{\varDelta E_1}{V_1} \right)^{\frac{1}{2}} \right]^2, \quad \ldots\ldots(1)$$

where $\bar{E}_2$ and E_2^0 represent, respectively, the partial molal energy and the molal energy of the pure solute. V_1, V_2 and $\varDelta E_1$, $\varDelta E_2$ are the molal volumes and the energies of vaporization of pure solvent and solute molecules, and n_2 and n_1 express the number of moles of the solute and solvent species. Since a regular solution is defined[4] by the relation,

$$\bar{S}_2 - \bar{S}_2^i = 0, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

that is, one in which no entropy change is involved when a small amount of one of its components is transferred from an ideal solution to it of the same composition, the total volume remaining unchanged,

$$\bar{E}_2 - \bar{E}_2^0 = \bar{F}_2^r - \bar{F}_2^i = RT \ln \frac{a_2}{N_2}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where $\bar{F}_2^r$ and $\bar{F}_2^i$ are the partial molal free energies of the solute in a regular and ideal solution ; a_2 is the activity and N_2 is the mole fraction of the solute in a regular and ideal solution, respectively. Furthermore, for a system in which a pure solid component is in equilibrium with its solution, the activity is equal to the mole fraction of the component in the solution, as is also the case in a system where the ideal solubility law is obeyed. Therefore,

$$\bar{F}_2^r - \bar{F}_2^i = RT \ln \frac{a_2}{N_2} = RT \ln \frac{N_2^i}{N_2}, \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

1) J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, 1, 817 (1933).

2) H. Menke, *Physik. Z.*, 33, 593 (1932).

3) A more rigorous statistical treatment of regular solutions is given by a) E. A. Guggenheim, *Proc. Roy. Soc.*, A 148, 304 (1935); b) J. G. Kirkwood, *J. Phys. Chem.* 43, 97 (1939).

4) J. H. Hildebrand, *J. Am. Chem. Soc.*, 51, 66 (1929).

where N_2^i* is the ideal solubility expressed in mole fraction. By introducing (4) in (1) the latter can be written,

$$RT \ln \frac{N_2^i}{N_2} = V_2 \left(\frac{N_1 V_1}{N_1 V_1 + N_2 V_2} \right)^2 \left[\left(\frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}} - \left(\frac{\Delta E_1}{V_1} \right)^{\frac{1}{2}} \right]^2 = V_2 \mathcal{V}_1^2 D^2, \dots\dots(5)$$

where $\mathcal{V}_1 = \left(\frac{N_1 V_1}{N_1 V_1 + N_2 V_2} \right)$ and $D = \left[\left(\frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}} - \left(\frac{\Delta E_1}{V_1} \right)^{\frac{1}{2}} \right]$, according to Hildebrand's notations. From equation (5) it is possible to calculate the solubility of a non-polar solid solute in non-polar liquids from the properties of the pure components involved. Often, it so happens that the values of the heat of vaporization at desired temperatures are not available or are not of sufficient accuracy. Usually, data on the heat of vaporization at the boiling point are more easily obtainable and more accurate. In the case of a solid, the heat of vaporization is commonly obtained from its vapor pressure, making use of the realation,

$$\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2} \dots\dots\dots(6)$$

The vapor pressure measurements are usually more reliable at higher temperatures. From these considerations, it is here proposed to use $\frac{a^{\frac{1}{2}}}{V}$[**] instead of $\left(\frac{\Delta E}{V} \right)^{\frac{1}{2}}$ to predict the solubility of a solid non-electrolyte in non-polar liquids.

In this paper a, the van der Waals constant, will be determined at *the boiling point* by making use of the relation,

$$a = V \Delta E. \dots\dots\dots(7)$$

where V and ΔE are, in this case, the molal volume and the energy of vaporization at *the boiling point*, respectively. a will be, in addition, assumed to be independent of temperature[5]. $\frac{a^{\frac{1}{2}}}{V}$ at any temperature can, then, be found by dividing the square-root of a by the molal volume at that temperature. By the use of the relation (7), equation (5) can be transformed into

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* N_2^i can be determined from the relation,

$$\frac{d \ln N_2^i}{dT} = \frac{\Delta L}{RT^2}$$

which on integrating becomes

$$\ln N_2^i = \frac{-\Delta L}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right)$$

where ΔL is the heat of fusion and T_m is the melting point of the solid. If ΔL is not independent of temperature, it can be expressed in terms of the difference of the heat capacities of the solid and liquid which are written as a function of temperature, and it is treated identically as above. In the calculations made in this paper, ΔL has been assumed to be independent of temperature. This assumption involves uncertainty in N_2^i smaller than that due to other factors.

** Hildebrand used the same relation but in his calculations a was obtained from the data at 25°C in most cases, and not at the boiling point. [see, Ref. 6; also J. H. Hildebrand, *J. Am. Chem. Soc.*, 57, 866 (1935).]

5) This assumption, though generally not strictly true over a wide range of temperatures, is to a

$$RT \ln \frac{N_2^i}{N_2} = V_2 V_1^2 \left[\frac{a_2^{\frac{1}{2}}}{V_2} - \frac{a_1^{\frac{1}{2}}}{V_1} \right]^2 \ldots\ldots\ldots\ldots\ldots(8)$$

Practical usefulness of equation (8) will be further demonstated[6].

In the results given below, $\frac{a_2^{\frac{1}{2}}}{V_2}$ has been calculated in two ways—1) from the solubility data of a solid in various non-polar (and some slightly polar, as indicated by their dipole moments) solvents ; 2) from the properties of the pure solid. It has been, furthermore, compared with $\left(\frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}}$ at the same temperature. The solid non-electrolytes taken for illustration are iodine, tin tetraiodide, sulfur, phosphorous, and biphenyl.

Iodine

The solubility of iodine in $SiCl_4$, $TiCl_4$, and $C_2H_4Br_2$ are taken from Negishi, Donnally, and Hildebrand[7] ; in benzene, CCl_4, and heptane from Hildebrand and Jenks[8] ; in hexane from Hildebrand, Ellefson, and Beebe[9] ; and in CS_2 and $CHCl_3$ from the International Critical Tables. To calculate the ideal solubility, N_2^i, the heat of fusion, 3740 calories per mole, a value recently determined by Frederick and Hildebrand[10], at its melting point, 114.1°C, is used. This gives $N_2^i = 0.2357^*$. Molal volumes and heats of vaporizations are taken either from the International Critical Tables or Landolt-Boernsteins Physikalisch-chemische Tabellen. Table I gives the results of $\left(\frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}}$ and $\frac{a_2^{\frac{1}{2}}}{V_2}$ calculated from the solubility data and from the properties of the pure solute.

Here, the agreement between $\left(\frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}}$ and $\frac{a_2^{\frac{1}{2}}}{V_2}$ calculated from the solubility data by the aid of the relations (5) and (8), respectively, and those calculated from the vapor pressure, that is, by making use of the relations,

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first approximation good for non-polar molecules ; since

$$a = \frac{N_0^2}{2} \int_{r_0}^{\infty} 4\Pi r^2 \left(\frac{3a\mu^2}{2r^6} \right) dr = N_0^2 \frac{\left(\frac{4}{3} \Pi^2 a\mu^2 \right)}{\frac{4}{3} \Pi r_0^3}$$

which is independent of temperature. In this equation N_0 is the Avogadro's number, a is the polarizability, μ^2 is the mean square dipole moment, r is the distance between the centers of molecules whose radius is $r_0/2$. (J. C. Slater, "Introduction to Chemical Physics," McGraw-Hill Book Co., 1939, page 411).

6) J. H. Hildebrand, "Solubility of Non-electrolytes," Reinhold Publishing Corporation, N. Y. (1936).

7) G. R. Negishi, L. H. Donnally, and J. H. Hildebrand, J. Am. Chem. Soc., 55, 4793 (1933).

8) J. H. Hildebrand and C. W. Jenks, ibid., 42, 2180 (1920).

9) J. H. Hildebrand, E. T. Ellefson, and C. W. Beebe, ibid., 39, 2301 (1917).

10) K. J. Frederick and J. H. Hildebrand, J. Am. Chem. Soc., 60, 1436 (1938).

* Hildebrand uses $\Delta l = 4010$ and obtains $N_2^i = 0.212$: see Ref. 6, page 153.

Table I
Iodine Systems at 25°C

Solvent	$\left(\frac{\Delta E_1}{V_1}\right)^{\frac{1}{2}}$	$\left(\frac{\Delta E_2}{V_2}\right)^{\frac{1}{2}*}$	$\frac{a_1^{\frac{1}{2}}}{V_1}$	$\frac{a_2^{\frac{1}{2}*}}{V_2}$
SiCl$_4$	7.57	13.76	7.60	13.81
CCl$_4$	8.54	14.10	8.35	13.91
TiCl$_4$	9.05	14.00	8.76	13.71
Benzene	9.00	13.10	8.93	13.03
CS$_2$	9.98	13.96	10.07	14.05
n-Heptane	7.45	13.40	7.30	13.25
n-Hexane	6.98	13.25	7.03	13.30
Chloroform	8.93	13.84	9.28	14.19
C$_2$H$_4$Br$_2$	9.68	13.18	10.05	13.55
Mean		13.62		13.65
Calculated from vapor pressure		13.56		13.71

* Calculated from solubility data.

$$\frac{\mathrm{d} \ln p}{\mathrm{d}T} = \frac{\Delta H}{RT^2} \text{ and } \Delta E = \Delta H - RT$$

is excellent.

Sulfur

The values of $\left(\frac{\Delta E_1}{V_1}\right)^{\frac{1}{2}}$ for the various solvents and $\left(\frac{\Delta E_2}{V_2}\right)^{\frac{1}{2}}$ for the solute, sulfur, are taken from "Solubility."[11] The heat of vaporization and the density neces-

Table II
Sulfur Systems at 25°C

Solvent	$\left(\frac{\Delta E_1}{V_1}\right)^{\frac{1}{2}}$	$\left(\frac{\Delta E_2}{V_2}\right)^{\frac{1}{2}*}$	$\frac{a_1^{\frac{1}{2}}}{V_1}$	$\frac{a_2^{\frac{1}{2}*}}{V_2}$
n-Heptane	7.45	12.3	7.30	12.15
CCl$_4$	8.54	13.2	8.35	13.01
Benzene	9.00	12.9	8.93	12.83
CS$_2$	9.98	11.7	10.07	11.79
Ether	7.45	12.0	7.50	12.05
Chloroform	8.93	12.9	9.28	13.25
Toluene	8.64	12.6	8.32	12.28
m-Xylene	8.10	11.8	8.47	12.17
CH$_2$Cl-CH$_2$Cl	9.08	13.5	9.65	14.07
CH$_2$Br-CH$_2$Br	9.68	13.5	10.05	13.87
Mean		12.8		12.77
Calculated from vapor pressure		11.7		12.46

* Calculated from solubility:

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11) Ref. 6, page 158.

sary for the calculation are from the usual sources, namely, the International Critical Tables and Landolt-Boernsteins Physikalisch-chemische Tabellen. The results of calculation are given in Table II.

The agreement between $\dfrac{a_2^{\frac{1}{2}}}{V_2}$'s calculated from the solubility data and that from the vapor pressure is better than that between $\left(\dfrac{\varDelta E_2}{V_2}\right)^{\frac{1}{2}}$'s.

Tin Tetraiodide

The solubility of SnI_4 in the solvents listed below, with the exception of $SiCl_4$ is taken from Dorfman and Hildebrand[12], and that in $SiCl_4$ is from Hildebrand and Negishi[13]. The heat of fusion, 4600 cal/mole at the melting point, 144.5°C, and the heat of vaporization which is calculated from the vapor pressure measurements on the liquid are taken from Negishi[14]. The vapor pressure in the temperature range 150 to 250°C is expressed by the relation,

$$\text{Log } p_{mm} = 7.6571 - \frac{2971.36}{T} - \frac{3689.1}{T^2} ,$$

and the heats of vaporization at the boiling point, 348°C, and at 25°C are 13,650 and 13,700 calories per mole, respectively. Table III gives the results of $\left(\dfrac{\varDelta E_2}{V_2}\right)^{\frac{1}{2}}$ and $\dfrac{a_2^{\frac{1}{2}}}{V_2}$.

The agreement between $\left(\dfrac{\varDelta E_1}{V_2}\right)^{\frac{1}{2}}$ and $\dfrac{a_2^{\frac{1}{2}}}{V_2}$ found from the solubility data and

Table III
Tin Tetraiodide Systems at 25°C

Solvent	$\left(\dfrac{\varDelta E_1}{V_1}\right)^{\frac{1}{2}}$	$\left(\dfrac{\varDelta E_2}{V_2}\right)^{\frac{1}{2}*}$	$\dfrac{a_1^{\frac{1}{2}}}{V_1}$	$\dfrac{a_2^{\frac{1}{2}}}{V_2}*$
$SiCl_4$	7.57	11.21	7.60	11.24
CCl_4	8.54	11.41	8.35	11.22
Benzene	9.00	11.44	8.93	11.37
n-heptane	7.45	10.89	7.30	10.74
Ether	7.45	10.77	7.50	10.82
Chlororm	8.93	10.71	9.28	11.06
Toluene	8.64	11.13	8.32	10.81
m-xylene	8.10	10.13	8.47	10.50
$C_2H_4Br_2$	9.68	11.64	10.05	12.01
Mean		11.15		11.08

Calculated from vapor pressure

	9.37			10.10

* Calculated from solubility data.

12) M. E. Dorfman and J. H. Hildebrand, *J. Am. Chem. Soc.*, **49**, 729 (1927).
13) J. H. Hildebrand and G. R. Negishi, *ibid.*, **59**, 339 (1937).
14) G. R. Negishi, *ibid.*, **58**, 2293 (1936).

those calculated from the vapor pressure is not as good as in the other two systems. This may be due, perhaps, to the uncertainty involved in the heat of vaporization, ΔH; since the extrapolation from the measured points is larger than in the others. Nevertheless, the agreement is tolerably good.

Phosphorous

The solubility data for phosphorous is taken from "Solubility"[16]. The heat of fusion, 584 cal/P_4, at the melting point, and the heat of vaporization expressed as,

$$\Delta H = 16350 - 7.106/T,$$

are taken from Smits and Bokhorst[16]. The density of the liquid is calculated from the relation,

$$d_t = 1.76705 - 0.0009222(t-20) \text{ from } 45.5 \text{ to } 80.6°C$$

given by Dobinski[17]. This gives, assuming the equation to be valid up to the boiling point, $v_2 = 81.28$ cc at the boiling point, 280.5°C, and 70.42 cc at 25°C. The ideal solubility, N_2^i, is calculated from the usual relation, using $T_m = 317$. It is 0.9463 at 25°C. Hildebrand[16] has used 625 cal/mole instead of the present value, 584, but the difference in N_2^i is negligibly small. In the table only those solutions at 25°C are given.

Table IV

Phosphorous System at 25°C

Solvent	$\left(\dfrac{\Delta E_1}{V_1}\right)^{\frac{1}{2}}$	$\left(\dfrac{\Delta E_2}{V_2}\right)^{\frac{1}{2}*}$	$\dfrac{a_1^{\frac{1}{2}}}{V_1}$	$\dfrac{a_2^{\frac{1}{2}*}}{V_2}$
Benzene	9.00	14.70	8.93	14.63
Ether	7.45	13.78	7.50	13.83
Calculated from vapor pressure		13.95		13.62

* Calculated from solubility data.

Biphenyl

The solubility data and the heat of fusion, 4235 cal/mole, are taken from Warner, Scheib, and Svirbely[18]. The molal volumes are calculated from the densities given by Montillon, Rohrbach, and Badger[19]. There is no reliable value for the heat of vaporization, so that a number of values of the heat of vaporization have

15) Ref. 6, page 163.
16) A. Smits and S. C. Bokhorst, Z. physik. Chem., 91, 249 (1916).
17) Dobinski, Z. Physik., 83, 129 (1935).
18) J. C. Warner, R. C. Scheib, and W. J. Svirbely, J. Chem. Phys., 2, 590 (1934).
19) G. H. Montillon, K. L. Rohrbach, and W. L. Badger, Ind. Eng. Chem, 23, 763 (1931).

been calculated from the vapor pressure measurements found in the literature.　They
are plotted as in fig. 1, and the value chosen is 11,8000 cal/mole at the boiling

Fig. 1
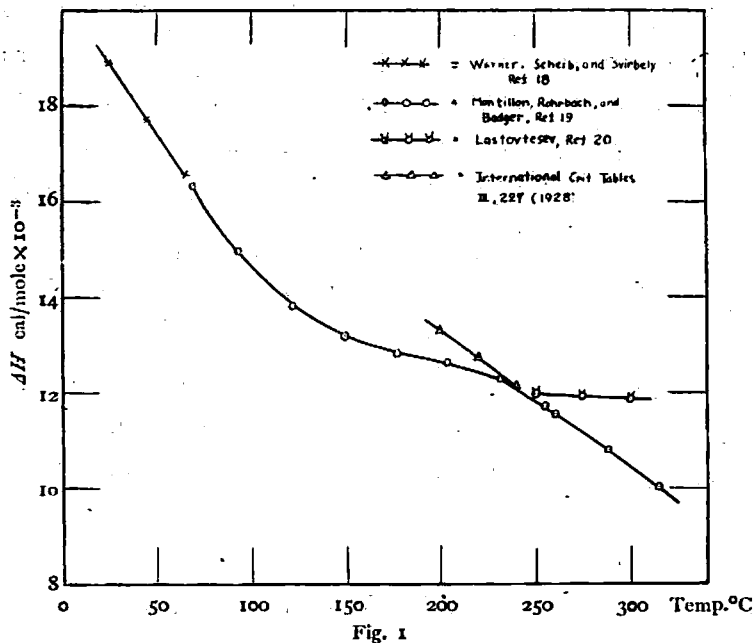
point, 255°C[20].　The ideal solubility has been calculated from the relation,[18]

$$\log N_2^i = -\frac{274}{T} + 4.38 \log T - 10.2996.$$

Table V

Biphenyl Systems at 45°C

Solvent	$\left(\frac{\Delta K_1}{V_1}\right)^{\frac{1}{2}}$	$\left(\frac{\Delta K_2}{V_2}\right)^{\frac{1}{2}*}$	$\frac{a_1^{\frac{1}{2}}}{V_1}$	$\frac{a_2^{\frac{1}{2}*}}{V_2}$
Benzene	8.81	10.15	8.79	10.13
CS$_2$	9.66	11.61	9.66	11.61
CCl$_4$	8.44	10.23	8.26	10.05
n-Heptane	7.20	9.65	6.92	9.37
Mean		10.41		10.26
Calculated from vapor pressure		10.61		9.27

*　Calculated from solubility data.

20) Montillon, Rohrbach, and Badger give 255.3°C, while A. M. Lastovtesev, (*Khim Mashinostro-enie*, **6**, 19 (1937); *Chem. Absts.*, **33**, 7634 (1936)) gives 253.7 when calculated from his vapor pressure equation (probably the one given below; we were unable to get the original),

$$\log p = 4.576 - \frac{2213.3}{(t+230)} \quad \text{(from 250°C to 400°C)}.$$

In Chem. Absts. and in Chem. Zentr., 1938 I, 1105 the equation is erroneously given as

$$\log p = 4.576 + 2213.3 \ (t+230) \text{ and}$$

$$\log p = 4.576 + \frac{2213.3}{(t+230)},$$

respectively; the International Critical Tables, III, 347 (1928) gives 254.9°C.

The results of $\left(\frac{\Delta E_2}{V_2}\right)^{\frac{1}{2}}$ ahe $\frac{a_2^{\frac{1}{2}}}{V_2}$ obtained are shown in Table V.

$\left(\frac{\Delta E_2}{V_2}\right)^{\frac{1}{2}}$ and $\frac{a_2^{\frac{1}{2}}}{V_2}$ in these systems are at 45°C, but the results are just as satisfactory as at 25°C—as expected. In this case, $\left(\frac{\Delta E_2}{V_2}\right)^{\frac{1}{2}}$ is in better agreement than $\frac{a_2^{\frac{1}{2}}}{V_2}$. If, however, ΔH would be 14.3000 instead of 11,800 or a difference of 2500 calories, $\frac{a_2^{\frac{1}{2}}}{V_2}$ would be 10.26, just the value found from solubility; or if ΔH is 13820 (a difference of 2000 cal.) the difference between the $\frac{a_2^{\frac{1}{2}}}{V_2}$'s calculated from the solubility data and the vapor pressure will be the same as that between the $\left(\frac{\Delta E_2}{V_2}\right)^{\frac{1}{2}}$'s. Uncertainty in the value of ΔH to this amount is entirely reasonable.

From the results of the tables we conclude that (a) if we have a several values of $\left(\frac{\Delta E_2}{V_2}\right)^{\frac{1}{2}}$ or $\frac{a_2^{\frac{1}{2}}}{V_2}$ determined from solubility, we can, then, predict with satisfactory accuracy the solubility of the solute in other non-polar liquids; (b) $\frac{a_2^{\frac{1}{2}}}{V_2}$ calculated from the energy of vaporization, employing the relation,

$$a = V\Delta E,$$

can predict with fair satisfaction the solubility of a solid non-electrolyte in non-polar liquids; (c) the assumption that a is independent of temperature is reasonable, as far as the solubility of solid non-electrolyes in non-polar (or slightly polar) liquids is concerned; (d) in a qualitative manner, the applicability of the relation, $a = V\Delta E$, and the consideration of (c) show that the change in the energy of vaporization is proportional to that of the volume[21].

Since the available data on the heat of vaporization are more abundant at the boiling point, and the vapor pressure measurement are relatively more accurate at higher temperatures, we believe that to calculate $\frac{a^{\frac{1}{2}}}{V}$ proves more useful than $\left(\frac{\Delta E}{V}\right)^{\frac{1}{2}}$ in many cases, and it can predict the solubility of a solid non-electroyte in non-polar liquids equally well as—if not better than $\left(\frac{\Delta E}{V}\right)^{\frac{1}{2}}$.

Summary.

$\left(\frac{\Delta E_2}{V_2}\right)^{\frac{1}{2}}$, the square root of the energy of vaporization per volume and $\frac{a_2^{\frac{1}{2}}}{V_2}$, the square root of the van der Waals constant, determined at the boiling point, divided by the molal volume of solid non-electolytes, iodine, stannic iodide, phosphorus, sulfur, and biphenyl in a number of non-polar and slightly polar solvents have been

21) J. H. Hildebrand, *J. Chem. Phys.*, **7**, 1 (1939).

calculated from the solubility data and from the physical properties of the pure components involved.

The agreement of $\left(\dfrac{\varDelta E_2}{V_2}\right)^{\frac{1}{2}}$ and $\dfrac{a_2^{\frac{1}{2}}}{V_2}$ between those calculated from the solubility data and from the vapor pressure of the pure solute has been found quite satisfactory.

Qualitatively, the results obtained have shown that the change in the energy of vaporization is porportional to that of the volume.

It has been suggested that to calculate $\dfrac{a_2^{\frac{1}{2}}}{V_2}$ rather than $\left(\dfrac{\varDelta E_2}{V_2}\right)^{\frac{1}{2}}$ may prove more convenient and useful in many cases.

It is the author's pleasure to acknowledge his appreciation to Professor Horiba for his interest in this paper.

The Central Laboratory,
South Manchuria Railway Company,
Dairen.