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Paper: C8T

Topic : Physical Chemistry-III

(a) Application of Thermodynamics – II

Colligative properties: (iv) Osmotic pressure] and amount of solute. Applications in calculating molar masses of normal, dissociated and associated solutes in solution; Abnormal colligative properties

Comments: The highlighted and the quoted portions are must read.

Reference:

Physical Chemistry by P.C. Rakshit

✓ XVII.8. Osmosis

In 1748, Abbé Nollet made the first striking observation that when a pig's bladder filled with alcohol and tied at the neck was kept immersed in water, it swelled enormously and ultimately burst. This is because the wall of the bladder is *semipermeable*, it allows water to get in but the alcohol cannot pass out.

In fact, there are membranes which are impervious to solute molecules but they allow solvent molecules to pass through them. These are called *semipermeable*

membranes. Pig's bladder, intestinal walls of some animals, the inner walls of egg-shells, the potato-skin etc. are semipermeable membranes. Collodion, gelatine films, cellophane films etc. are also semipermeable. The best semipermeable membrane commonly used now is a layer of precipitated copper ferrocyanide deposited on a porous wall.

Now if a solution and pure solvent be kept separated by means of a semipermeable membrane, the solvent molecules only will pass through the membrane into the solution in order to dilute it. This phenomenon of diffusion of a solvent through a semipermeable membrane from the solvent to a solution or from a dilute solution to a concentrated one is called osmosis. Since the solute cannot diffuse through the membrane, nature tends to achieve equilibrium through osmosis. It is understood that the passage of solvent occurs in both directions, but the diffusion of the solvent from the solvent to the solution is much more rapid than that in the opposite direction.

✓ An easy demonstration can be made by tying a stretched piece of bladder or cellophane across the mouth of an inverted thistle funnel. It is filled with conc. sugar solution and kept partly immersed in water as in Fig. XVII.9. Slowly the liquid inside will rise and finally the level becomes stationary. This is because due to osmosis, the water from outside enters through the membrane, but when the hydrostatic pressure counterbalances the force which causes the water to diffuse from outside, the eqm. is attained and the level becomes stationary.

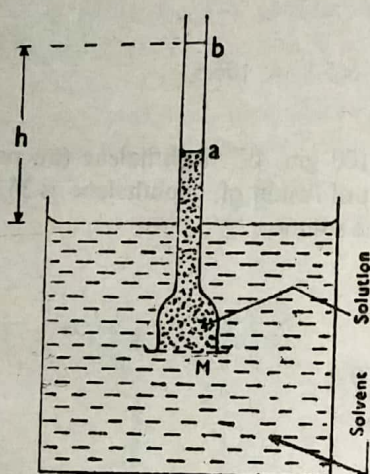


Fig. XVII.9

Other illustrations of osmosis may be cited. When a dry prune is placed in water, it swells as water enters through the semipermeable skin of the fruit. The hard outer shell of an egg may be removed by carefully dissolving it in dil. HCl. If the egg is then placed in water, it swells. On the other hand, if the egg is placed in very conc. solution of a salt, the egg shrinks. The thin membrane beneath the hard shell is semipermeable.

Red blood cells when placed in a strong solution are found to shrivel when observed under microscope. But they swell and burst when kept in a very dilute solution, which is the cause for *haemolysis*.

XVII.9. Osmotic Pressure

Let us have a U-tube, as in Fig. XVII.10, provided with a semipermeable partition at the centre X. One arm of the tube is filled with a solution and the other with pure solvent. There are piston arrangements for applying pressures on the liquids. Normally solvent will pass through X into the solution i.e., osmosis will occur. This diffusion of the solvent into the solution through the membrane can be counteracted by applying pressure π over the solution. The excess pressure π on the solution that would just prevent osmosis is called the osmotic pressure of the solution. The term is somewhat misleading, for a solution by itself cannot exert any pressure due to osmosis. The osmotic pressure of a solution is the pressure required to prevent osmosis when the solution is separated from pure solvent by a semipermeable membrane.

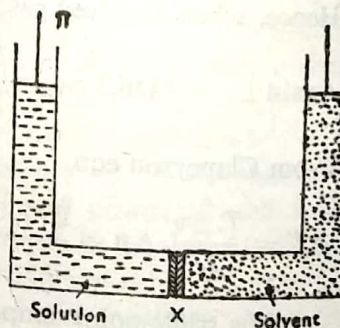


Fig. XVII.10
Osmotic pressure

When eqm is established between the two sides of the membrane the rates of diffusion of the solvent in the two opposite directions will be the same. The magnitude of the osmotic pressure depends on various factors such as temperature, concentration etc., but it is not dependent on the nature of the membrane provided it is perfectly semipermeable. Hence, although the membrane makes the osmotic

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pressure manifest, it is not the cause of the osmotic pressure. The osmotic pressure is a result of difference in the thermodynamic potentials of the solvent and the solution.

XVII.11. Laws of Osmotic Pressure

The wealth of data which accumulated from the experiments of Pfeffer, of Morse and Frazer, of Berkeley and Hartley and their co-workers led to certain very interesting conclusions. It was realised quite early that the osmotic pressure of solutions depends upon both the temperature and the concentration of the solutions. Quantitatively these were formulated into the following laws:

LAW 1. *Temperature remaining constant, the osmotic pressure (π) of a solution is directly proportional to its concentration (C).*

$$\pi = k_1 C, \quad (k_1 \text{ is a constant})$$

Since $C = 1/v$, where v litres contain 1 gm-mole of solute,

$$\pi = k_1/v \quad \text{or} \quad \pi v = k_1$$

LAW 2. *Concentration remaining constant, the osmotic pressure (π) of a solution is directly proportional to absolute temperature (T)*

$$\pi = k_2 T, \quad (k_2 \text{ is a constant})$$

It is evident that these two laws are analogous to the Boyle's and Charle's laws for gas-pressures. Below are appended some experimental data which establish the validity of these laws.

TABLE: OSMOTIC PRESSURE OF SUCROSE SOLUTIONS (15°C)

Conc. in gms per 100 gms	π (osmotic pressure) mm of Hg	π/C
10	535	535
20	1016	508
40	2082	521
60	3075	513

TABLE: OSMOTIC PRESSURE OF SUCROSE SOLUTIONS (0.1 molal)

Temp. ($T^{\circ}\text{K}$)	π (osmotic pressure)	$\pi/T (\times 10^3)$
273	7.085	2.594
283	7.334	2.591
293	7.605	2.595
298	7.729	2.594

The two laws enunciated above may be combined, so as to give the relation

$$\pi = CKT,$$

when both temperature and concentration would vary. K is a constant. If the solution contains n gm-moles of solute in V litres of solution, we have

$$\pi = \frac{n}{V}KT \quad \text{or} \quad \pi V = nKT. \quad \dots \text{(XVII.12)}$$

It may then be stated: "Equimolecular quantities of different solutes dissolved in the same volume of a solvent exert equal osmotic pressure at the same temperature." It is presumed that the solutes are supposed not to suffer dissociation or association in the solution. This is sometimes mentioned as the third law for osmotic pressures.

As equimolecular quantities contain the same number of molecules, the above statement may be expressed alternatively: "Equal volumes of different solutions which are at the same temperature and exert same osmotic pressure contain an equal number of solute molecules." This is indeed Avogadro's law applied to solutions. The osmotic pressure is thus dependent on the number of molecules and independent of their nature. So it is a colligative property.

The remarkable identity of equation (XVII.12) with the ideal gas equation was pointed out by van't Hoff.

Ideal gas equation:

$$PV = nRT$$

Osmotic pressure equation:

$$\pi V = nKT$$

When the experimental values of π were substituted in equation XVII.12, the numerical value of K was found to be 0.082 litre-atmosphere/degree, the same as that of " R " of the gas equation. Equation XVII.12 for solutions now becomes, (C is the molar concentration of the solute in the solution),

$$\text{or} \quad \left. \begin{array}{l} \pi V = nRT \\ \pi = CRT \end{array} \right\} \quad \dots \text{(XVII.13)}$$

Van't Hoff therefore rightly stated: "The osmotic pressure of a substance in solution is the same as it would exert if it existed as a gas in the same volume as that occupied by the solution at the same temperature." The solution is dilute and the volume occupied by the solute in solution is negligible compared to the volume of the solution.

This is generally called van't Hoff's law of osmotic pressure, which is really a combination of the separate laws stated earlier.

✓ XVII.12. Osmotic Pressure from Thermodynamic Considerations

Suppose a solution A is kept separated from the pure solvent B by the semi-permeable membrane X as in Fig. XVII.13.

The concentration of the solvent is x_1 mol-fraction and that of the solute x_2 mol-fraction. The temp. is kept constant throughout.

Let the pressure initially over both the solvent and the solution be P_0 .

μ_1^0 = Chemical potential of the solvent in the pure state under pressure P_0 and μ_1 = Chemical potential of the solvent in the solution under the same pressure P_0 .

In order just to prevent osmosis, the pressure over the solution is raised to P . Then, the osmotic pressure (π) is

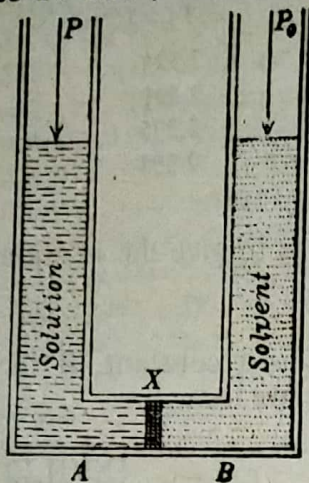


Fig. XVII.13
Osmotic Pressure

$$\pi = P - P_0 \quad \dots (i)$$

Let $\mu_1(s)$ be the chemical potential of the solvent in the solution under pressure P . At equilibrium, the chemical potentials of the solvent in the solution and in pure state must be the same, i.e.,

$$\mu_1(s) = \mu_1^0 \quad \dots (ii)$$

Now, under the pressure P_0 , the chemical potential (μ_1^0) of the pure solvent is changed to μ_1 due to the presence of solute (Sec. VII.33).

$$\text{Hence} \quad \mu_1 = \mu_1^0 + RT \ln x_1 \quad \dots (iii)$$

Again, in the given solution, the chemical potential of the solvent is μ_1 under pressure P_0 and it changes to $\mu_1(s)$ under pressure P , hence (See. eqn VII.36),

$$\mu_1(s) = \mu_1 + \int_{P_0}^P \left(\frac{\partial \mu_1}{\partial P} \right)_T dP = \mu_1 + \int_{P_0}^P \left(\frac{\partial \bar{G}_1}{\partial P} \right)_T dP$$

Since $\left(\frac{\partial \bar{G}_1}{\partial P} \right)_T = \bar{V}_1$, where \bar{V}_1 is the molar volume of the solvent which is supposed to remain the same in dilute solutions,

$$\text{We have,} \quad \mu_1(s) = \mu_1 + \int_{P_0}^P \bar{V}_1 dP$$

$$\text{or} \quad \text{Substituting (iii) in (iv),} \quad \mu_1(s) = \mu_1 + \bar{V}_1 (P - P_0) = \mu_1 + \bar{V}_1 \pi \quad \dots (iv)$$

$$\mu_1(s) = \mu_1^0 + RT \ln x_1 + \bar{V}_1 \pi$$

But from (ii), $\mu_1(s) = \mu_1^0$, hence, $\pi \bar{V}_1 + RT \ln x_1 = 0$

$$\text{or} \quad \pi \bar{V}_1 = -RT \ln x_1 = -RT \ln (1 - x_2)$$

As in dilute solution, x_2 is small, $\ln (1 - x_2) \approx -x_2$

$$\therefore \quad \pi \bar{V}_1 = RT x_2 \quad \dots (XVII.14)$$

$$\text{Rewriting,} \quad \pi = \frac{RT}{\bar{V}_1} \frac{n_2}{n_1 + n_2} \approx \frac{RT}{\bar{V}_1} \cdot \frac{n_2}{n_1} = RT \cdot \frac{n_2}{v}$$

where v = total volume of the solvent and n -terms are the respective gm-moles.

$$\text{Therefore,} \quad \pi = RT c_2 \quad \dots (XVII.15)$$

as already found in eqn. XVII.13.

XVII.13. Osmotic Pressure and other Colligative Properties

The inter-relations between the different colligative properties of dilute solutions can be easily formulated.

$$(a) \text{ From eqn. XVII.14, } \pi \bar{V}_1 = x_2 RT$$

or

$$x_2 = \pi \bar{V}_1 / RT = \pi M_1 / \rho RT \quad \dots (XVII.16)$$

(M_1 = mol. wt. and ρ = density of the solvent)

From Raoult's Law, $x_2 = \Delta P/P_1^0$

Hence,
$$\frac{\pi M_1}{\rho RT} = \frac{\Delta P}{P_1^0} \quad \dots \text{(XVII.17)}$$

(b) The elevation of b. pt. (ΔT_b) is

$$\Delta T_b = k_b \cdot \frac{\omega_2 \times 1000}{M_2 \times \omega_1} = k_b \cdot \frac{n_2 \times 1000}{n_1 \times M_1} = k_b \cdot \frac{1000}{M_1} x_2$$

Substituting x_2 from (XVII.16),
$$\Delta T_b = k_b \cdot \frac{1000}{M_1} \cdot \frac{\pi M_1}{\rho RT} = \frac{k_b \times 1000}{\rho RT} \pi$$

or
$$\pi = \frac{\rho RT}{k_b \times 1000} \cdot \Delta T_b \quad \dots \text{(XVII.18)}$$

Similarly,
$$\pi = \frac{\rho RT}{k_f \times 1000} \Delta T_f \quad \dots \text{(XVII.19)}$$

The colligative properties of dilute solutions are extensively employed for determination of mol. wts, especially the depression of freezing-point and elevation of boiling-point. If ω_2 gms of solute be present in ω_1 gms of a solvent (mol. wt. M_1), the different colligative properties are, (where $M_2 =$ mol. wt. of the solute),

1. Vapour pressure lowering,
$$\frac{\Delta P}{P_1^0} = \frac{n_2}{n_1 + n_2} = \frac{\omega_2/M_2}{\omega_1/M_1 + \omega_2/M_2}$$

2. Boiling-pt. elevation,
$$\Delta T_b = k_b \cdot \frac{\omega_2 \times 1000}{\omega_1 \times M_2}$$

3. Freezing-pt. depression,
$$\Delta T_f = k_f \cdot \frac{\omega_2 \times 1000}{\omega_1 \times M_2}$$

4. Osmotic pressure,
$$\pi = CRT = RT \cdot \frac{\omega_2/M_2}{v}$$

Since, the lowering of vapour pressure, osmotic pressure, elevation of b. pt. and depression in f. pt. can be measured with reasonable accuracy, M_2 can be evaluated from the equations noted above. When the solute is volatile, molecular weight determination by vapour-pressure lowering or boiling-point elevation would not be suitable.

Problem. A solution contains 0.6 gm urea and 1.8 gm glucose in 100 c.c. of water at 27°C. Calculate the osmotic pressure of the solution.

Now conc. per litre = $6/60 + 18/180 = 0.2$

$\therefore \pi = 0.2 \times .082 \times 300 = 4.92$ atm.

Problem. At 100°C the vapour pressure of a solution of 6.5 gm of a solute in 100 gm water is 732 mm. What is the boiling pt. of the solution? ($K_b = 0.52$). Assume the laws of dilute solution.

At 100°C, for pure water $P_0 = 760$ mm

$$\Delta P = P_0 - P = 760 - 732 = 28 \text{ mm}$$

Hence
$$\frac{n_2}{n_1} = \frac{\Delta P}{P_0} = \frac{28}{760}$$

Now
$$\Delta T_b = K_b \cdot \frac{\omega_2 \times 1000}{\omega_1 \times M_2} = k_b \cdot \frac{n_2 \cdot 1000}{n_1 M_1}, \text{ (Since } n_2 = \frac{\omega_2}{M_2}; w_1 = n_1 M_1)$$

$$= 0.52 \times \frac{28}{760} \times \frac{1000}{18} = 1.064^\circ$$

\therefore The boiling-pt. of the solution, $T_b = 101.064^\circ\text{C}$

Problem. Calculate the freezing point of a solution of cane sugar which has an osmotic pressure of 5 atmospheres at 50°C.

From equation (XVII.19),

$$\pi = \frac{\rho RT \Delta T_f}{1000 \times K_f} = \frac{1 \times 82 \times 323 \times \Delta T_f}{1000 \times 1.86}$$

or

$$\Delta T_f = \frac{5 \times 1.86}{0.082 \times 323} = 0.352, \text{ (using } R \text{ in c.c. atm, as } \rho \text{ is gm/cc.)}$$

The freezing pt. of the solution is -0.352°C .

XVII.14. Abnormal Behaviour of Solutions

The experimental results for the colligative properties of solutions are often at variance with the values calculated from the relations mentioned above. This is due to two reasons:

- (i) The solutions are often not ideal, especially at higher concentrations. The non-ideality leads to abnormal results.
- (ii) The association or dissociation of solute molecules in solution also lead to departure from theoretical expectations.

Non-ideality in solutions: The laws for dilute solutions are basically derived from the Raoult's law, $p_i = x_i p_i^0$. Raoult's law is valid for ideal solutions only. But real solutions obey Raoult's law only at high dilutions. At higher concentrations, the solutions exhibit considerable departure.

(The element of non-ideality enters into the picture when the molecules of the solute and the solvent affect each others' intermolecular forces or if there be association or complex-formation between the solute and the solvent. These become quite conspicuous at higher concentrations and the experimental results become abnormal.)

Association in Solution. Some solutes when dissolved in non-hydroxylic solvents like benzene, cyclohexane, carbon-tetrachloride, nitrobenzene etc. remain associated. Thus, carboxylic acids like acetic acid, benzoic acid etc. remain mostly as dimers in benzene solution. Evidence of the existence of association has also been found in the results of partition coefficient experiments. The association would render the number of solute particles less than what it would have been if the solute were present as single molecules. The properties of dilute solutions, being colligative in nature, depend on the number of solute particles and not on their chemical composition. In consequence, the values of osmotic pressure, freezing point depression, boiling point elevation etc. would be less than those theoretically anticipated from the relations derived for them. The molecular weight calculated from the observed freezing point lowering or boiling point elevation etc. in such cases would obviously be higher. The observed values for the mol. wt. of acetic acid obtained from freezing point depression are given in the table here, which shows that except in very dilute solutions, the molecular weight is nearly double that of its chemical formula (mol. wt. 60).

TABLE: OBSERVED MOL. WT. OF ACETIC ACID IN BENZENE SOLUTION

Molality	ΔT_f (°C)	Obs. mol. wt.	$\frac{M_{obs}}{M_{theo}}$
0.003	0.016		
0.015	0.054	65.8	1.09
0.097	0.254	84.5	1.41
0.510	1.252	117.0	1.95
1.025	2.410	114.5	2.07
		130.2	2.17

It is clear that at very high dilutions only acetic acid remains as single molecules in benzene solutions; at low dilutions most of the acid remain as dimers. At fairly high concentration, the molecules associated even exceeds 2. This is due to the fact that apart from association, the solution also shows positive deviation from Raoult's law to some extent.

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The degree of association can also be evaluated. Suppose α is the degree of association *i.e.*, the fraction of total solute present as dimers of mol. wt. $2M_0$. Then $(1-\alpha)$ fraction would remain as single molecules of mol. wt. M_0 . If M is the mean (observed) mol. wt., then

$$M \left(1 - \alpha + \frac{\alpha}{2} \right) = 2M_0 \left(\frac{\alpha}{2} \right) + M_0(1-\alpha)$$

or
$$\alpha = \frac{2(M-M_0)}{M} \dots \text{(XVII.20)}$$

If n molecules are associated, instead of 2, the degree of association would similarly be given by,

$$\alpha = \frac{n(M-M_0)}{M(n-1)} \dots \text{(XVII.21)}$$

The finding of a higher value for mol.-wt. from a colligative property does not necessarily mean association of the solute molecules in solution. This may be illustrated in the case of nitrobenzene.

TABLE: OBSERVED MOL. WT. OF NITROBENZENE IN BENZENE SOLUTION

($M_{theoretical} = 123$)

Molar Conc.	$\Delta T_f(^{\circ}\text{C})$	M_{obs}	$\frac{M_{obs}}{M_{theo}}$	Molar Conc.	$\Delta T_f(^{\circ}\text{C})$	M_{obs}	$\frac{M_{obs}}{M_{theo}}$
0.286	1.632	129.7	1.06	0.735	3.950	143.7	1.15
0.496	2.720	137.0	1.11	1.180	6.230	152.7	1.35

The observed mol. wt. increases with higher and higher concentrations and does not tend to reach a constant value. There is also no other evidence or indication pointing towards association of nitrobenzene molecules in solution. It is very likely that the deviations from the normal value are due to the non-ideality of the solution arising out of the difference of intermolecular forces in each of solute and solvent.

Dissociation in Solution. In 1885, van't Hoff found that dilute aqueous solutions of electrolytes such as NaCl, MgSO_4 etc. show a considerable departure from the ideal. The observed osmotic pressure of solutions of salts of known concentration (C) was found to be much higher than that predicted from the relation, $\pi = CRT$. As a result the mol. wt. calculated from the observed osmotic pressure is much less than that from the chemical formula of the solute. Van't Hoff did not offer any explanation for the abnormal results, but introduced a factor, i , to contain the deviations from ideal equation in case of solutions of electrolytes, expressing

$$\pi_{ideal} = CRT, \quad \pi_{observed} = iCRT \dots \text{(XVII.22)}$$

Therefore,
$$i = \frac{\pi_{obs}}{\pi_{theo}} \dots \text{(XVII.23)}$$

The van't Hoff's factor " i " is thus the ratio of the observed osmotic pressure and the ideal osmotic pressure.

It was further found that for a given solution of an electrolyte the deviation in any colligative property would be the same as that in osmotic pressure, *i.e.*,

$$i = \frac{\pi_{obs}}{\pi_{theo}} = \frac{\Delta T_{f(obs)}}{\Delta T_{f(theo)}} = \frac{\Delta T_{b(obs)}}{\Delta T_{b(theo)}} = \frac{\Delta P_{obs}}{\Delta P_{theo}} \dots \text{(XVII.24)}$$

In high dilutions, " i " tends to the numerical value 'two' for electrolytes like NaCl, MgSO_4 , HNO_3 , etc. For electrolytes like H_2SO_4 , CoCl_2 etc. the value approaches 'three'; for $\text{K}_3\text{Fe}(\text{CN})_6$, the value tends to 'four' and so on.

TABLE: VAN'T HOFF FACTOR ' i ' FROM OBS. ΔT_f , FOR DIFFERENT ELECTROLYTES

Electrolyte	Molality			
	1.00	0.1	0.01	0.001
NaCl	1.81	1.87	1.94	1.97
HCl	2.12	1.89	1.94	1.98
CuSO ₄	0.93	1.12	1.45	—
HNO ₃	1.92	1.89	1.96	1.97
H ₂ SO ₄	2.17	2.12	2.46	2.82
CoCl ₂	—	2.62	2.75	2.90
Pb(NO ₃) ₂	1.31	2.13	2.63	2.89
K ₃ Fe(CN) ₆	—	2.85	3.36	3.82

The explanation of the abnormal colligative properties of solutions of electrolytes comes readily from the Arrhenius dissociation theory. According to the dissociation theory, the electrolyte molecules in solution break up into positive and negative ions. In very high dilutions, the dissociation is complete. Thus in dilute solutions, p molecules of NaCl will give rise to $2p$ ions; p molecules of H₂SO₄ will give $3p$ ions and so on. Since the colligative properties depend on the units of solute present in solution irrespective of their chemical nature and because, due to ionisation the number increases, the values of the colligative properties observed are much higher. In fact, these results from the dilute solutions gave the strongest and most dramatic support to the Arrhenius theory of dissociation.

Generally speaking, suppose a molecule breaks up into n ions in a given solution of concentration c . If a is the degree of dissociation, then

$$\text{conc. of undissociated molecules} = (1-a)c$$

$$\text{and conc. of (dissociated) ions} = n.a.c$$

$$\text{Hence total conc. of solute particles} = c[1 + n-1a]$$

The osmotic pressure of such a solution, $\pi_{obs} = c[1 + (n-1)a]RT$. But from eqn. (XVII.24) van't Hoff's corrected equation is, $\pi_{obs} = i.cRT$

Hence

$$i = 1 + (n-1)a$$

or

$$a = \frac{i-1}{n-1}$$

... (XVII.25)

As ' i ' is experimentally determined from freezing pt. measurement or measurement of other colligative properties, a is known. The degree of dissociation determined in this way is found to be practically the same as obtained from conductance measurements. Such identity confirms the explanation given above.)