On the Nature of Ionic Sign Preference in C. T. R. Wilson Cloud Chamber Condensation Experiments

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Experiments made to ascertain if the charge preference in the C. T. R. Wilson cloud method of condensation was due to different hygroscopic impurities brought into the embryonic droplets by capture of ions of different sign proved definitely negative. Since the electrical double layers at liquid-gas surfaces are also incapable of explaining the phenomenon the following hypothesis was evolved and compared to existing experimental data together with results obtained for the first time on $C_6H_5NO_2$, C_6H_5Cl, C_4H_9Br, $C_6H_5CH_3$, $C_6H_5NH_2$ and new results on C_2H_6CO, C_6H_6 and C_2H_5I. It is assumed that the saturated vapor contains *embryonic droplets* of radius insufficient to bring surface tension forces into play. These droplets unlike the larger and more stable visible and invisible droplets are in a *state neither crystalline nor liquid but in a pseudo-crystalline state* having definite space structure. In such pseudo-crystalline or embryonic droplets the orientation of the molecules is determined by van der Waals forces which are directive. As in Thomson's theory at lower supersaturation the nascent surface tension forces preclude growth beyond a certain size. Capture of gaseous ion as in Thomson's theory facilitates condensation by adding dielectric attractive forces. If, the droplet and vapor consist of polar molecules whose dipole moment is oriented in such a direction as to bring approaching vapor molecules to the pseudo crystal surface in an orientation favorable to further structural growth the sign of charge favoring this process will produce visible droplets at a lower supersaturation than will the opposite sign. Once condensation has proceeded to a point where surface tension forces are fully developed the droplet goes over to the *liquid* state having an electrical double layer and neither sign of charge have any further influence on condensation. Using as the directive forces in condensation primarily hydrogen bond formation and dipole attraction the effects observed experimentally can be accounted for on plausible assumptions as to linkage in the embryonic drops. The reason that gaseous ions are not observed to grow to these droplets can be ascribed to the fact that these are already stable complex ions of very few molecules whose orientation is not that of the pseudo-crystals. A capture of such an ion by a pseudo-crystal of 10^2 to 10^5 molecules will not, however, affect the pseudo-crystal other than to facilitate condensation. It is believed possible that it is these pseudo-crystalline droplets or groupings existing in liquids that account for the cybotatic state described by G. W. Stewart from x-ray studies. In gases it is possible that they constitute the intermediate atmospheric ions when large enough to survive the acquisition of a charge. The larger or Langevin ions are then probably the nucleii once formed by supersaturation and condensation to visible size and which have subsequently re-evaporated to invisible liquid droplets with surface tension forces active (10^7 or more molecules) that have acquired a charge. The three groups of ions mentioned exist independently with charged carriers of sizes lying between them entirely absent except during the unstable conditions producing transition.

INTRODUCTION

WHEN C. T. R. Wilson[1] made his early studies on the cloudy condensation produced by ions in a gas, he discovered that with water vapor the condensation occurred at lower expansion ratios for negative ions than for positive ions. Przibram[2] later observed that in some substances, for example, ethyl alcohol, the condensation occurred more readily on the positive ion. While the subsequent work confirmed the sign preference, the results were mostly quite discordant.[3-5] The causes of the discrepancy may be sought for in one or several of the following factors:

1. Differences in the degree to which adiabatic expansion was achieved.

2. Failure to correct for the influence of the vapor of the substance in calculating supersaturation.

3. Lack of uniformity and control of the purity of the substance used.

4. No clearly defined common criterion for the appearance of condensation. This is extremely important as the work of Andren[6] and the present work show.

[1] C. T. R. Wilson, Phil. Trans. Roy. Soc. **A189**, 265 (1897); **A193**, 289 (1899). J. J. Thomson, Phil. Mag. **36**, 313 (1893).

[2] K. Przibram, Ber. d. Königl. Akad. Wiss. Wien, **II a 115**, 23, 1906, **II a 118**, 331 1909. Also for later discussion and references see Geiger and Scheel, *Handbuch der Physik*, second edition, Vol. 22, part 1, p. 418 ff.

[3] F. G. Donnan, Phil. Mag. **3**, 305 (1900).

[4] T. A. Laby, Phil. Trans. Roy. Soc. **A208**, 445 (1908).

[5] *International Critical Tables*. Vol. VI (1926), p. 117.

[6] L. Andren, Ann. d. Physik **52**, 1 (1917).

5. Failure to study a sufficient diversity of substances with a uniform technique to enable the nature of the process to be analyzed.

Although the phenomenon of sign preference has thus long been known and utilized in the early determinations of e,[7] its character is completely obscure. In an endeavor to understand the mechanism, investigations suggested by tentative hypotheses were undertaken by us. In these, some of the difficulties in previous work came to light. No attempt was made to make exhaustive or careful redeterminations or to correct the past errors. Enough data, however, have been accumulated, when taken with negative evidence from other fields to lead us to propose a radical but seemingly plausible theory.

The theory for the condensation in the cloud chamber experiments propounded by J. J. Thomson[8] is as follows: Saturated vapor contains numbers of minute nuclei of condensation. Adequate supersaturation causes these to increase by condensation. As they reach a size where the forces of surface tension become fully developed, the curvature of the surface inhibits further condensation, unless the supersaturation exceeds a certain value. For water at room temperatures this occurs at eightfold "supersaturation" as defined by C. T. R. Wilson. Between fourfold and eightfold supersaturation, the droplets do not grow to visible size. If, however, the droplets acquire a negative charge above fourfold supersaturation condensation occurs. Positive charges require about a sixfold supersaturation. The visible droplets must have a diameter of about 10^{-5} cm. This action is due to the forces of dielectric attraction *in* the water droplet, which counteract the effect of the curvature of the surface. It is not open to more than a semi-quantitative verification at the present time.

In its original form, the theory assumed that the water droplets *grew about the ions* by condensation. As early as 1917, Loeb[9] showed that this assumption was purely gratuitous. All that the theory requires is that the embryonic droplets acquire a charge in order that they grow.

The charge can be acquired in an ionized gas just as Millikan's oil drops acquired charges.

It must be noted that this mechanism does *not* account for sign preference, since the dielectric action of the charge in the drop is *independent* of its sign. The following hypotheses have been at one time or another considered as accounting for sign preference:

1. That the ions have a specific affinity for vapor molecules which is sign dependent. That the condensation begins *about* the ions and that as ions grow, the one with the strongest affinity grows faster. This implies that the affinity manifests itself for drops that are of considerable size.

2. That there is an electrical double layer in the surface of the drop with one sign of charge outside and the other inside. A charge on the drop which orients approaching vapor molecules so as to combine with this layer will favor the condensation. The opposite charge will hinder this process. The nonpreferential electrostatic forces of the charge acting on the drop in Thomson's equation act independently of the double layer. In his third edition, J. J. Thomson proposes such a double layer. He, however, places one sign of charge *in the gas phase* and the other in the drop.

3. That the gas ions being electrochemical complexes, analogous to complex ions in solution, carry into the embryonic droplets besides the charge some of their companion molecules.[10] If the type of companion carried by one sign of ion into the embryo lowered its vapor tension, more than did the companion carried by the opposite ion, one might expect a difference in condensing power. That is, it was believed possible that the few impurity molecules carried into droplets by ions might add the effect of a concentrated solution in lowering the vapor tension of the droplets.

Since, as will later be seen, there was strong evidence against the first and second of these explanations, experiments were undertaken with a view to ascertaining the real extent of the sign preference and to determining whether hygro-

[7] J. J. Thomson, Phil. Mag. **46**, 528 (1898); **48**, 547 (1899).
[8] J. J. Thomson, *Conduction of Electricity Through Gases*, third edition, Vol. 1 (Cambridge 1928), pp. 320–333.
[9] L. B. Loeb, J. Frank. Inst. **182**, 790 (1917).

[10] L. B. Loeb, Summary in *Kinetic Theory of Gases*, second edition (McGraw-Hill, New York, 1934), Section 106, p. 564 ff. Also Phys. Rev. **32**, 81 (1928); **38**, 549 (1931), and Bradbury, Phys. Rev. **38**, 1716 (1931). See also Tyndall and Phillips, Proc. Roy. Soc. **A111**, 577 (1926); Loeb and Dyk, Proc. Nat. Acad. Sci. **15**, 146 (1929). Herbert Mayer, Physik. Zeits. **27**, 513 (1926); O. Luhr, Phys. Rev. **44**, 459 (1933); **28**, 637 (1927).
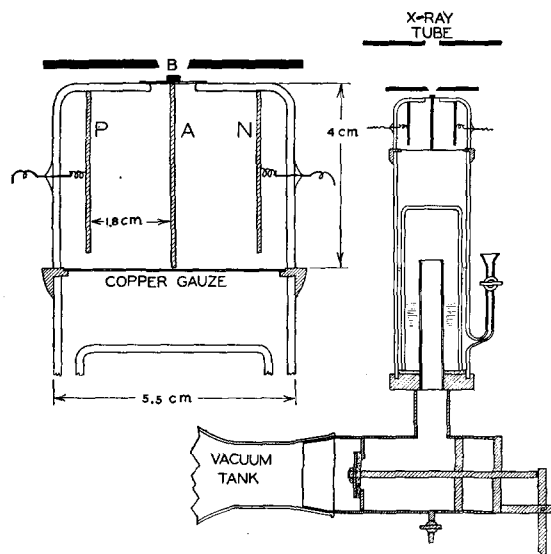
FIG. 1.

scopic impurities carried into drops by the ions could be of any influence as suggested under hypothesis 3.

EXPERIMENTAL PROCEDURE AND RESULTS

The technique was essentially that employed by C. T. R. Wilson.[1] The design of the cloud chamber is shown in Fig. 1. Expansion was effected by means of a glass plunger which was floated in the liquid to be tested. On opening the valve to the vacuum tank the air was removed from beneath the glass plunger, causing it to be forced down onto a rubber washer with such speed as to make the expansion process essentially adiabatic. The presence of the metal parts makes realization of adiabatic expansion more difficult. For most of the liquids other than water, the rubber washer was replaced by Thiokol, an artificial rubber which is resistant to many organic substances, including most of those tested. In operation, the gas is ionized by a narrow beam of x-rays in the central section by a flash from the x-ray tube. A lead block B prevents the x-rays from striking the central electrode A. A thin aluminum window is provided for the entrance of the x-rays. The two copper plates, P and N, are respectively positive and negative with respect to A to a degree sufficient to draw the negative ions out towards P and the positive ions out towards N. At the

proper time the measured adiabatic expansion is effected, giving a nearly nonturbulent region between A, N, and P. The nature of the expansion ratio for the condensation on positive and negative ions and that for general cloudy condensation can then be determined. For if the time interval between ionization and expansion and the electrical field are correct, only positive ions exist in the region near N and negative ions in the region near P. For water, the potential required between the center plate and N and P was ±1.5 volts; for other substances such as C_2H_5I it was as high as 50 volts. The potentials on P and N were reversed to avoid any errors due to lack of symmetry of the x-ray beam. The time interval between x-ray flash and expansion for most complete separation of positive and negative ions used at these voltages was about one second. *The criterion for onset of condensation was taken as the lowest expansion ratio which gave a definite cloud, as contrasted to the 5 or 10 scattered drops which are nearly always present near the critical expansion ratio.* The measurements on pure water in hydrogen and air are detailed below. The measurements made on other substances are summarized in Table I.

Most of the substances used were of the best C.P. grade available. Earlier results indicated no essential effect of impurities on sign preference, while impurities did change the values of the expansion ratios. Hence, greater purity was not sought. Subsequent results on C_6H_6 showed that where high expansion ratios and slight or no sign preference occur, impurities can materially alter the supersaturation needed and give a sign preference. Accordingly the greater precautions were used in the C_6H_6 and $C_6H_5CH_3$ experiments. Filtered air and tank H_2 were used, and later tank N_2, two months old, replaced air, since it was free from all nuclei. The chamber was also rebuilt to permit of ready and complete cleaning. For some substances N_2 cannot be used as N_2 does not give negative ions and electrons are swept out too rapidly.

The expansion ratios were calculated in the standard manner, care being used in each case to correct for the vapor pressure of the substance used as given in the *International Critical Tables*. These values were not available to earlier workers and may account for some of the dis-

crepancies. The values for pure water agree fairly well with those of other workers, notably Przibram. For all other substances except acetone, the ratios observed were in general higher than those obtained by previous workers. While this could be attributed to a slower adiabatic expansion or greater warming by the metal parts, the agreement in water seems to preclude an instrumental effect. The chamber used should in fact have given a more rapid expansion than those used by other workers. In some cases the gradual increase in the number of droplets with expansion ratio was sufficiently slow so as to cause a considerable latitude in the choice of the expansion ratio for condensation. For alcohol this is not the case, and the higher ratio observed here might be ascribed to a higher purity of alcohol in view of the fact that water lowers the expansion ratio materially. This is clearly shown by pure benzene, C_6H_6, b.p. 80.2°, which gave an expansion ratio on ions of both signs, of 2.15. When contaminated with 20 percent commercial C_6H_6, the ratio was 1.89 on ions with a negative charge.*

In view of the various factors influencing the absolute values of the observed expansion ratios too much emphasis cannot be placed on the significance of the absolute values in any work of this sort. It is, however, believed that the relative values especially for different signs of charge are correct and most significant.

REALITY OF SIGN PREFERENCE AND THE EFFECT OF IONIC CONTAMINATIONS

Very carefully purified and boiled water was introduced into the clean chamber and the expansion ratios for condensation on positive and negative ions were determined in air and in pure H_2. While the ratios obtained in H_2 for condensation on positive and negative ions differed slightly from the values in air, it was found that in both cases condensation occurred ·at lower expansion for negative ions than for positive ions. The difference in the expansions in air and H_2 can be attributed entirely to the difference in the specific heats of the two gases. That is, the necessary supersaturation was very likely the

same in the two cases, though this cannot be accurately verified. Since in air it is known that the positive and negative ions pick up different chemically active impurities formed by x-rays, while in H_2 no such substances other than H_2O_2 and perhaps O_2 can be formed, it seems reasonably sure that the sign preference was *not alone* due to a difference in hygroscopic impurities picked up by the positive and negative ions.

This was further confirmed by a study of mixtures of HCl and water. HCl vapor is hygroscopic and HCl is soluble in water. It lowers the vapor pressure of H_2O and makes definite complexes with the *negative* ion presumably containing more than one molecule.[11] Even positive ions make smaller complexes with HCl. Yet none of the solutions of HCl up to concentrations of 23 percent, (i.e., above the constant boiling mixture concentration) that were used showed a decrease in the expansion ratio required for either sign of ion. It was found, however, that mixtures of acetic acid and water did condense on both ions at *lower ratios* than did either vapor separately. A similar effect had been observed in the case of alcohol—water mixtures, initially by Przibram[2] and later by others.[12] These effects are thermodynamically to be expected for acetic acid and alcohol.[12] The effects in alcohol are greater than those observed in acetic acid although the latter are pronounced. In mixtures of acetic acid and water vapors, the former showing sign preference for positive the latter for negative ions, no sign preference is observed since the general lowering of the expansion ratio by mixing probably masks the small differences observed.

It was observed that both acetic acid and HCl were made particularly troublesome by the formation of nuclei *after ionization and a condensation of droplets on the ions*. These nuclei were in a large measure uncharged and persisted after being formed until diffusion and repeated expansion removed them. The character of these nuclei was pointed out by J. J. Thomson.[8] If through ionization and condensation by adequate expansion droplets are formed, they re-evaporate to an invisible size on warming up. The size reached corresponds to the bottom of the second

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* This has since been shown to be due to water. 10 percent of C_6H_6 saturated with H_2O causes such an effect.

[11] L. B. Loeb, Proc. Nat. Acad. Sci. **12**, 35, 42 (1926).
[12] Volmer and Flood, and H. Flood, Zeits. f. physik. Chemie **A170**, 273 and 286 (1934).

minimum in the surface tension supersaturation curve of Thomson. Here the droplets remain as stable but invisible droplets. Due to the ambient ionization they in time lose their charges but do not further evaporate for at this size the drop is stable without charge. In fact, charges only influence the growth at much *smaller* sizes. On the slightest increases of supersaturation by adiabatic expansion, these invisible stable droplets again quickly grow to visible size. If ions all of one sign were present about these drops, they would persist as large ions, and it is probable that the Langevin ions found in the atmosphere are of this character. The *persistence* of the nuclei in the presence of HCl and C_2H_5COOH is notable and doubtless due in the case of the HCl to the concentrated solutions of HCl in the larger but invisible droplets (lowered vapor pressure) while in C_2H_5COOH water mixtures it is due to the fact that the expansion ratio for all condensations is less, as shown by Vollmer and Flood.[12] It is clear, however, that *the few HCl molecules or active hygroscopic molecules introduced into embryonic nuclei before the first condensation through diffusion or gaseous ions does not materially influence the condensation process.* In other words, as will appear probable later, the elementary condensation nuclei or *embryonic droplets* are in a different physical state and thus act differently from the larger stable nuclei which have their surface tension forces fully active.

The signal failure of the third proposed mechanism led the writers to cast around for a more plausible theory. J. H. Hildebrand in conference suggested that in addition to the surface layer structure of liquids and the dipole moments, one must study the type of linkages resulting from secondary valence forces between molecules in the condensation processes. The writers then undertook a program of the study of sign preference among a varied assortment of condensable liquids. The scope of such a study is small in that the experiments must be limited to liquids capable of being condensed by realizable expansion ratios in the gases used. Up to the time of this study, water was the only substance showing a negative sign preference. This work has added $C_6H_5NH_2$, CH_3I, C_6H_5Cl, and $C_6H_5CH_3$ to the molecules showing negative sign preference. The results observed are summarized in Table I,

which is largely self-explanatory. The symbols E and E_0 are the *expansion ratios* observed for condensation with ions of *both* signs, and for general cloudy condensation in the absence of ions respectively. The symbols E_+ and E_- are the expansion ratios for condensation with positive and negative ions. The *ratios* are given since the rather unusual definition of "supersaturation" introduced by C. T. R. Wilson has little significance. The temperature was 22°C throughout.

DISCUSSION OF PROPOSED THEORIES

1. The idea that molecules condense about the ions on supersaturation can be led back to the old notion of the ion cluster, as a bulky group of molecules attracted by dielectric forces. Work in the last ten years has conclusively shown that ions are not such agglomerations.[10, 13] They consist in the main of a few (one to four) molecules showing marked sign preference for the charge on the ion and are akin to the well known complex ions in solution. Thus, for example, the negative ion has an affinity for alcohols ROH, Cl_2, HCl, etc., while the positive ion has a strong affinity for NH_3, RNH_2, ethyl ether, etc.[10] With various partial pressures of vapors, including water vapor, only one ionic mobility is observed which shows no indications of being a cluster that alters with the partial pressure of the vapor. Similar results are observed in the unique mobility peaks produced in spraying and bubbling of liquids. Hence one is forced to conclude that ions do not "grow" into drops and that the presence of charge on droplets that condense is due to the picking up of the ions by the drops.

The conclusion based on observation is to be expected since there is no *a priori* reason for believing that molecular affinities for ions of one sign are in any way related to the van der Waals forces linking molecules in condensation. This is strikingly illustrated in a few cases by reference to the tables. CH_3I has no specific ionic affinity yet it shows negative sign preference in condensation. H_2O shows negative sign preference and the alcohols show a marked positive sign preference while all of them have a strong affinity for nega-

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[13] Powell and Brata, Proc. Roy. Soc. **A138**, 129 (1932).

tive ions. Amines have a strong affinity for positive ions yet $C_6H_5NH_2$ condenses more readily on negative ions. Finally, it seems unlikely, even did the charge affinity exist, that it would extend over sufficient drop radii to influence condensation.

2. Studies of spray electrification by Lenard[14] and his pupils, cataphoresis of gas bubbles,[15] direct potential measurements by Frumkin,[16] static charge production on separation of surfaces by Coehn,[17] and surface adsorption experiments by Langmuir[18] and others are all in agreement in establishing the existence of the electrical double layers at the surface of liquids. The character of these double layers is not definitely known and the best information comes from

[14] P. Lenard, Ann. d. Physik 47, 463 (1915). See also H. W. Gilbert and P. E. Shaw, Proc. Phys. Soc. (London) 37, 195 (1925).

[15] McTaggart, Phil. Mag. 27, 297 (1914); 28, 367 (1914). Also T. Alty, Proc. Roy. Soc. A106, 313 (1914).

[16] Frumkin, Zeits. f. physik. Chemie 109, 34 (1914); 111, 190 (1914); 116, 485 (1920); 123, 321 (1926).

[17] A. Coehn, Wied. Ann. 64, 217 (1898). Coehn and Mozer, Ann. d. Physik 43, 1048 (1914).

[18] I. Langmuir, J. Frank. Inst. 218, 143 (1934).

spray electrification and bubbling. Coehn and Mozer[17] have studied these layers in liquids other than water by bubbling, as have Blüh[19, 20] and recently Chapman[21] in this laboratory. Chapman's results are in general agreement with those of Blüh but the correlation of his results with the results of Coehn and Mozer is doubtful because of the rather primitive nature of the earlier measurements and due to the fact that he studied the more recently formed carriers. From their own results Coehn and Mozer believe they have proved the law of Coehn that each pure liquid has an electrical double layer at the surface the *negative charge being outward*. The intensity of the field increases in proportion to the dielectric constant. Thus Coehn explains surface electrification on contact or friction as the result of a contact potential the substance with the highest dielectric constant always being positive. Chapman's recent results on spray

[19] Blüh, Kolloid Zeits. 59, 346 (1932).

[20] Blüh and Stark, Zeits. f. Physik 43, 575 (1927).

[21] S. Chapman, Phys. Rev. 52, 184 (1937).

TABLE I. *No ± effect.*

NAME	FORMULA	E	E_0	DIPOLE MOMENT $\times 10^{18}$	FIELD NECESSARY
Benzene (pure)	C_6H_6	2.15±.04		2.2	±1.5v Very sensitive to impurities.
Benzene	C_6H_6	1.73		0	±1.5v
Nitrobenzene	$C_6H_5NO_2$	1.45		3.9	±1.5v
Chloroform	$CHCl_3$	1.83	2.06	1.05	±4.5, ±1.5v
Acetone	$(CH_3)_2CO$	1.88		2.80	
Acetic acid	$+H_2O$	1.24	1.33	same for 50 per cent and 6.2 percent solutions	±4.6v

Negative ion first

NAME	FORMULA	E_-	E_+	E_0		FIELD NECESSARY
Water	H_2O	1.25	1.31	1.32	1.85	±1.5v
Ethyl iodide	C_2H_5I	1.82	2.11		1.66	±50v
Analine	$C_6H_5NH_2$	1.44	1.48		1.56	±25v
Chlorobenzene	C_6H_5Cl	1.53	1.6	1.8	1.52	±4.6v
Toluene	$C_6H_5CH_3$	1.60	1.69	1.73	0.4	±4.6v
$HCl+H_2O$		1.27	1.3	1.37	same for all conc.	17.5 percent 19 ±1.5v 23 (fuming) very weak

Positive ion first

NAME	FORMULA	E_-	E_+	E_0		FIELD NECESSARY
Ethyl alcohol	C_2H_5OH	1.29	1.26		1.70	±1.5v
Methyl alcohol	CH_3OH	1.37	1.33	1.58	1.68	±1.5v
Acetic acid	$C_3H_4O_2$	1.54	1.45		1.4	±3.0v
n-butyl bromide	C_4H_9Br		1.48		1.85	±25v

electrification throw some doubt on this interpretation. Both spraying and bubbling experiments show that many very mobile negative ions are found as well as definite groups of slower ions, while sometimes two and perhaps three groups of slower positive ions appear. Both positive and negative carriers as well appear in an added very broad band of large charged droplets. In ethyl alcohol similar results are observed to those in water but with nearly ten times the number of charged carriers. In a heavy saturated pure hychrocarbon, Nujol, no charged carriers are observed to any extent. Both nitrobenzol and aniline show no carriers of high mobility of either sign but both show a continuous band of large ions with equal numbers of positive and negative ions. These results are not such as one would expect on Lenard and on Coehn's predictions. Since Coehn's general law seems well established on other grounds the apparent contradiction of Chapman's results with the conclusions of Lenard and Coehn may be ascribed to faulty conclusion as to the origin of spray electrification rather than to the nonexistence of double layer. However, as will be seen from the table of results for sign preference, the very definite and widely differing behavior of the various substances studied allow of *no correlation with either Chapman's results or with Coehn's law.* Thus, with Chapman alcohol and water show similar behavior and aniline and water differ radically, while water and aniline act in a similar fashion in condensation and water and alcohol show opposite sign preference on condensation. If Coehn's law gave a clue to the surface orientation active in condensation it would be expected that the condensation would always occur preferentially on negative ions, since the negative outer layer of all liquids would more readily bind the positive ends of dipoles. These data definitely indicate that the usual electrical double layer existing at the surface of liquids is not responsible for sign preference in condensation. There is still the possibility envisaged by Thomson[8] that the charge itself causes an orientation at the surface of the liquid, which differs with the sign of charge. If it did occur, however, the orientation by the charge on the liquid surface and of approaching gaseous dipoles outside the liquid surface would for both

charges be in a proper sense to *aid* condensation, giving no sign preference.

3. The third alternative was shown by our experiments to be untenable.

THE EXPLANATION OF SIGN PREFERENCE

It is clear that sign preference depends on the sign of the charge on the droplet. It appears unlikely that this will materially alter the character and orientation of molecules bound by van der Waals forces in the drop. If it did so, the action unless unusual in its character would not lead to sign preference. The electrical fields existing at the surface of the charged embryonic droplets are of the order of 10^5 to 10^4 volts per cm. Such fields are definitely capable of orienting the *approaching* vapor molecules if they have in them strong permanent dipole moments. If then the structural aspect presented by such an oriented molecule is favorable to linkage with surface molecules, it is clear that such a vapor molecule is in a favored condition for condensation. The oppositely oriented molecule will *not be so favorably situated if the surface is unchanged by the charge.* To utilize this orientation of the vapor dipoles in the field of the drop for an explanation of sign preference, two things are required: 1. that the *axes of the dipole moments have definite directions in the molecules relative to the atomic configurations which determine the linkage elements in the van der Waals binding forces*; 2. that the *surface molecules of the embryonic droplets have definite orientations which will insure the outward propagation of the drop structure on the addition of molecules from the vapor.*

The studies of dipole moments and chemical structure have given us considerable knowledge as to the general relation of the dipole axis to the molecular structure in some cases.[22] More information can be had at will. As to linkage elements in the van der Waals forces little unfortunately is known. The excellent studies of solubilities as reported by Hildebrand[23] in his recent book are beginning to give us some information. It is clear that the hydrogen bond

[22] P. Debye, *Polar Molecule* (Hirzel, Leipzig, 1929). C. P. Smyth, *Dielectric Constant and Molecular Structure* (Chemical Catalog Co., New York, 1931). H. A. Stuart, *Molekulstructur* (Springer, Berlin, 1934).
[23] J. H. Hildebrand, *Solubility* (Chemical Catalog Co., New York, 1936). Also Science **83**, 21 (1936).

formation is one of the most powerful forces active. This occurs especially in the cases of F, O, and N atoms combined with H. Whether it occurs in smaller measure for other halogens remains an open question. Next to bond formation as active agents in linkage Hildebrand lists dipole linkages. In these cases the orientation of the dipoles linking is antiparallel. For most organic dipoles the substituent group is in general negative. A third group of forces active according to Hildebrand is the London forces. In this the linkage of dipoles is parallel and the linkage is strongest for the alkyl iodides. As regards the condensation studies it is probable that the London forces are not of great importance since they are not such as to propagate a structure. Where it is possible, there is no doubt but that the hydrogen bond will predominate. In its absence the antiparallel dipole linkage in chain structures may occur. The lack of specific knowledge of the relation between linkage axes and dipole axes for most molecules leave the specific interpretation of results open only to speculation. On the basis of solubilities Hildebrand did predict that nitrobenzol would show no sign preference and that amines would show a negative sign preference.

As regards the molecular orientation in drops, little can be said. Drops which are *large enough to have a well defined surface layer will show the ordinary statistically conditioned electrical double layer with little surface orientation.* Such a layer it was seen, cannot be of any significance. It is at this point that we must make a radical assumption. It must be assumed that the sign preference occurs on *embryonic droplets which are too small to take on the thermodynamical character of an aggregate with a regular surface layer.* It must also be assumed that these *embryonic droplets have a pseudo-crystalline structure* such that linkages inside the structure are manifest at the surface, and that these are unaffected by the charge that is picked up from the gas. The linkages are thus more of the nature of crystalline structures than of liquids. These droplets presumably do not pick up foreign molecules that do not enter into the structure. Where they can do so as in acetic acid and water, or alcohol and water mixtures, they are picked up and contribute to the lowering of the condensation ratio. Indications that such

aggregates exist even in the liquid state might be seen in the cybotactic structure revealed by the x-ray liquid diffraction studies of G. W. Stewart.[24] The existence of a pseudo-crystalline state of possibly similar character has been observed in the case of very minute Bi crystals by Goetz.[25] The size of such aggregates must run from 5×10^{-8} to 10^{-6} cm and contain 100 to 10^6 molecules. When the droplets exceed this size, the structure breaks down and a regular liquid droplet results. This picture will require a slight modification of the Thomson theory for the effect of charge on the growth of the droplets, over the first hump in the curve to the first minimum, in that ordinary thermodynamical considerations are inapplicable to the smaller embryonic drops with few molecules. The breakdown of this part of the theory is in any case indicated by sign preference. The reason why *ions* do not themselves grow to droplets is that they are already a stable complex of few molecules which do not share the structure of the larger embryonic pseudocrystals. It must be emphasized that this discussion *does not preclude* the action of the usual electrical forces, which Thomson and others show important in later stages. It does indicate that there is an earlier stage of the process where sign preference occurs in which ordinary electrical attraction does not suffice.

Rules Governing Charge Preference in Condensation

On the basis of these general considerations one may make certain definite predictions as to the condensation phenomena.

1. Where there is no permanent dipole moment there will be no sign preference on condensation.

2. Where the dipole moment is so oriented that the field of an embryonic pseudo-crystalline droplet is able to orient the approaching vapor molecules into a position favorable for a given type of surface linkage with the oriented molecules in the surface one sign of charge will

[24] G. W. Stewart, Phys. Rev. **37**, 9 (1931).
[25] A. Goetz, Papers and Discussions, International Conference on Physics, London, Vol. 2 (Cambridge Press, 1934), p. 65. Anniversary volume of Science Reports. Tohoku Imperial University, Series I. Sendai, Japan (1936).

facilitate condensation more than the other. Condensation will occur at lower expansion ratios on the ion of one sign than the other.

3. The presence of a strong permanent dipole moment in a molecule may not insure sign preference in condensation. It must in addition fulfill the following conditions.

a. The dipole direction in the molecule must be structurally so oriented as to facilitate the binding linkage in the molecules. Thus, for instance, a dipole moment axis perpendicular to the linkage groups would be of no advantage in condensation.

b. The dipole moment must not be so buried in a highly polarizable structure as to lose its influence in orienting the molecule in the divergent field near the surface of the embryo droplets.

c. The surface molecules must be oriented in sufficient numbers materially to affect the rate of condensation, a condition which obtains only in the minute pseudo-crystalline embryonic droplets.

4. The orientation produced by the field must be such as to cause linkages which are already present in the surface structure. That is, they must act to facilitate the addition of successive layers of molecules on the subjacent ones with the same structure as the subjacent ones. Thus it is conceivable that a field could orient molecules so as to saturate the linkage possibilities of the outer layer and thus prevent further growth. Hence dimer formation which occurs for many dipolar molecules in solvents (e.g. in the case of acetic acid where molecules link in pairs) cannot be of any value in the processes envisaged.

APPLICATION OF THEORY TO SPECIFIC VAPORS

It is now possible to turn specifically to the results reported in the table under the heads of: *a*, no sign preference, *b*, preference for negative ions, *c*, and preference for positive ions. The application to specific vapors can only be speculative; accordingly only illustrative examples will be given for each class.

a. No sign preference

As expected, benzene C_6H_6 having no dipole moment shows no preferential condensation. Nitrobenzol and acetone both have very strong

dipole moments but neither shows any sign preference. The behavior of nitrobenzol was predicted by Hildebrand from solubility data on the basis of its dipole being unrelated to its structural binding points. Acetone was tried before its solubility characteristics had been investigated. Its behavior is found to be in agreement with what the solubility data led one to expect. Chloroform has a dipole moment but shows no sign preference for the reason that its dipole is so effectively buried in the highly polarizable Cl_3 structure as to be ineffective.

CS_2, a nonpolar substance, was found by Przibram to show no sign preference.

b. Negative sign preference

The first case of sign preference observed in condensation was the negative sign preference shown by C. T. R. Wilson to hold for water vapor. Since the structure of the pseudo-crystalline state is not known, one is free to choose a structure consistent with condensation data. Since hydrogen bond formation is known to be the linkage and preference in condensation is for negative ions, one must conclude as follows: The O molecules in the pseudo-crystals must be outward. Then a negative charge on the pseudo-crystal will orient approaching H_2O molecules with the protons towards the surface favoring hydrogen bond linkage. Molecules striking a positively charged pseudo-crystal will have to rearrange themselves on impact with the surface to be bound. There is some indication of this orientation in the structure of ice crystals.

At the time the present investigations were undertaken water was the only vapor showing preference for condensation on negative ions. Owing to the use of low sweeping fields in the condensation chamber in working with vapors where the ions have a low mobility ethyl iodide was reported erroneously by an earlier investigator as having a sign preference for positive ions. By using adequate fields to separate the ions it was clearly shown that ethyl iodide has a distinct sign preference for negative ions. Data for the orientation of ethyl iodide in surfaces is not at hand. According to Hildebrand the London forces are powerful in alkyl iodine compounds. As these are probably not active here it might be suspected that in general the molecule will

have some sort of tetrahedral symmetry about the carbon atom holding the I. In a surface both the C_2H_5 group and the I because of space occupation might be expected to orient outward. Since linkage on condensation will presumably occur with the one of the two hydrogens of the carbon atom attaching to the iodine atoms at the surface, a negative charge on the ion will facilitate such combination. Aniline was found to have negative sign preference. Toluene and chlorobenzene were also observed to favor the negative ion. These three substances are characterized by organic chemists as being strongly *ortho-para* directive and it may be that this tendency is also manifested in the condensation process. It is, however, more profitable to speculate further as follows:

The structure of aniline is pyramidal and presents many possible methods of combination. The bulky C_6H_5 group might be thought of as projecting outward from the surface in which case it is possible that the C_6H_5 may be the linking group. However, the fact that hydrogen bond formation is possible makes it more likely that the N atom is outward in the droplet surface with the protons of the NH_2 inward. Then the hydrogens of the NH_2 of the condensing molecules which will be oriented downward by the field of a negative ion will favor linkage of the H with the nitrogen at the surface.

c. Positive sign preference

Perhaps the greatest difficulty at first encountered in interpreting these phenomena came in the behavior of the alcohols and fatty acids. On the basis of the action of H_2O the alcohols should be expected to show negative sign preference. Reflection will at once show why this is not the case. Hydrogen bond linkage is active here. However, the alcohols will orient with the organic radical or carbon chain outward where possible. In this case it is clear that the negative oxygen will point inward while the carbon chain and the H group are oriented outward. Thus the linkage will be facilitated by condensation on the positive ion, which orients the oxygen group of the approaching vapor molecule downward favoring hydrogen bond formation.

The Inhibition of Homogeneous Organic Decompositions

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A free radical mechanism is proposed to account for the inhibition of organic decompositions by nitric oxide, based on the assumption that the nitric oxide can both start and stop reaction chains in the substrate. Propylene inhibits organic decompositions and a free radical mechanism appears to account for this effect also. Ethyl nitrite completely inhibits the oxygen promoted chain in acetaldehyde at 300°C but has only a relatively small effect at 500°C.

(1) INTRODUCTION

A FREE radical mechanism such as that proposed by one of us[1] leads to the conclusion that two organic compounds when mixed do not decompose independently of each other and consequently we would expect the experimental result that the rate of decomposition of a particular compound would be either accelerated or retarded by addition of another compound. Acceleration of reaction rate has been observed in a large number of examples[2] but retardation of the rate is much less common; Hinshelwood and his co-workers have found that nitric oxide inhibits

[1] (a) Rice, J. Am. Chem. Soc. **53**, 1959 (1931); (b) Rice and Herzfeld, ibid **56**, 284 (1934); (c) Rice and Rice, *The Aliphatic Free Radicals* (The Johns Hopkins University Press, 1935).

[2] (a) Frey, Ind. Eng. Chem. **26**, 200 (1934); (b) Sickman and Allen, J. Am. Chem. Soc. **56**, 1251 (1934); (c) Echols and Pease, J. Am. Chem. Soc. **58**, 1317 (1936).