at 20° is 6.3 mm. It is also evident from Fig. 1 that the vapor-pressure measurements on the saturated solution of Rochelle salt show that the solid phase in such a solution is unstable above 40° as previously pointed out by van Leeuwen. The fact that the points obtained with decreasing temperature in the transition range fall on a different curve from that obtained with increasing temperature in the same range indicates that equilibrium had not been reached.

Summary

Vapor pressures of Rochelle salt, the hydrates of sodium tartrate and potassium tartrate, and their saturated solutions have been determined by a static method at several temperatures between 15° and 40°.

New York, N. Y.

[Contribution from the Chemical Laboratory of Clark University, I, 34]

THE RADICAL THEORY IN MODERN CHEMISTRY[1]

By Charles A. Kraus

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In a compound containing a large number of atoms a corresponding number of valence bonds exist among the constituent atoms. In the reaction of such compounds not all the valence bonds, in general, break down; but more often a few, or even a single bond, may break down with the formation of new compounds in which some of the original combinations remain. The different valence bonds in a compound thus have varying degrees of stability, and those atoms which are joined by the more stable bonds remain combined with one another throughout a series of reactions. These relatively stable groups are what are commonly termed radicals. It is the purpose of the present paper to determine in how far the properties of compounds may be interpreted in terms of those of the more stable groups from which these compounds are built up.

I have shown elsewhere that the properties of compounds of the binary type may be interpreted in terms of the electro-affinities of the constituent elements.[2] With respect to their electro-affinities, the elements may be arranged in a series from the most electropositive to the most electronegative. This series is a twofold one since, with the exception of the very electropositive and the very electronegative elements, all elements may carry negative as well as positive charges, and thus appear in both series. These elements appearing in both series, which have been termed amphoteric elements, comprise the major portion of the elements, and the

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[1] This paper comprises the subject matter of the Nichols Medal Address delivered before the New York Section of the American Chemical Society, on March 7, 1924.

[2] Kraus, *Trans. Am. Electrochem. Soc.*, **45**, 379 (1924).

properties of their compounds can be interpreted only when we take into account the electrical condition of the elements.

It is known that certain groups act as strongly electropositive ions while others act as strongly electronegative ions, and it may be inferred that groups of intermediate electro-affinity exist possessing amphoteric properties. The properties of the compounds of these groups with other groups or with elements are primarily determined by the electro-affinities of the constituent groups and elements. But it is to be borne in mind that the properties of the group in its compounds, as well as those of the compounds in which that group may occur, depend upon the state of charge (positive or negative) of the group in question.

Below are arranged in series a number of well-known groups, the positive electro-affinities diminishing from left to right or the negative from right to left.

SERIES OF ELECTRO-AFFINITIES OF SOME GROUPS

← (+)									
$N(CH_3)_4$	NH_4	CH_3Hg	CH_3	$C(C_6H_5)_3$	$Sn(CH_3)_3$	Strongly negative			
· Strongly		CH_3Hg	CH_3	$C(C_6H_5)_3$	$Sn(CH_3)_3$	CN	ClO_4	SCN	NO_3
positive			Amphoteric groups			(−) →			

The groups on the extreme left are known only in the electropositive condition and those on the extreme right only in the electronegative condition, while the intermediate groups are known in the electronegative as well as the electropositive condition. The physical as well as the chemical properties of the elements are primarily determined by their electro-affinities. Correspondingly, the properties of the groups in the free condition are determined by their electro-affinities. In general, the properties of the groups, both physical and chemical, should correspond closely with the properties of elements of the same electro-affinity. Because of the complexity of the various groups and the reactivity of their constituent elements, it is to be expected that many of them will not be stable in the free state. Nevertheless, a sufficient number of these groups is known in this state to indicate that their properties closely resemble those of corresponding elements.

The strongly electronegative groups are formed by the combination of two or more strongly electronegative atoms. They are non-polar compounds which are extremely reactive toward more electropositive elements or groups, but only weakly reactive toward strongly electronegative elements. The thiocyanogen group (SCN), isolated by Söderbäck,[3] is a typical example of a group of this type.

The strongly electropositive groups approach the strongly electropositive elements in their properties. The ammonium group is the commonest example of this type of group. The constitution of these groups

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[3] Söderbäck, *Ann.*, **419**, 219 (1919).

corresponds to the formula $R_{n+1}M^n$ where R is hydrogen or a univalent organic group and M is an element of the 5th, 6th or 7th group of the periodic system of normal valence n. We thus have, for example, the ammonium, sulfonium and iodonium groups. The quaternary alkyl ammonium group has been obtained as a stable amalgam[4] at low temperatures, while in liquid ammonia the group forms a blue solution[5] which appears to be identical with corresponding solutions of the alkali metals. The stability of the free groups of this class is not great, owing to the fact that they contain elements which possess a marked affinity for the negative electron and reaction in general occurs according to the equation: $2R_{n+1}M^n = 2R_nM^n + R_2$.

The groups which occupy an intermediate position in the series of electro-affinities are relatively stable in the free state. They are reactive toward positive as well as negative elements and they form bimolecular compounds in solution at higher concentrations. Triphenylmethyl is a typical example of this type of group.[5a] In general, these groups are derived from the elements of the 2nd, 3rd and 4th groups of the periodic system and their constitution corresponds to the formula $R_{n-1}M^n$, where n is the normal valence of the element M, and R is a univalent organic group or hydrogen. Elements of the 5th and higher groups of the periodic system also form free groups corresponding to the same formula, n being the valence with respect to hydrogen. Thus we have groups of the type R_2N.

While these groups are usually non-metallic in the free state, in a few instances in which the central atom, M^n, is sufficiently electropositive the free group is metallic. Thus the groups $HgCH_3$, HgC_2H_5 and HgC_3H_7 are metallic substances which exhibit metallic luster when in coherent form.[2] They decompose at ordinary temperatures according to the equation: $2RHg = R_2Hg + Hg$. Groups of the type $R_{n-1}M^n$ resemble hydrogen more closely than they do any other element. This is in part due to the fact that hydrogen is the only univalent element occupying an intermediate position in the series of electro-affinities. The carbon groups, such as methyl and phenyl, belong to this class. They are characterized by the fact that they form comparatively stable bimolecular compounds, in which respect they resemble hydrogen.[6]

Let us now consider the compounds of the different types of groups.

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[4] McCoy and Moore, THIS JOURNAL, **33**, 273 (1911).

[5] Palmaer, *Z. Elektrochem.*, **8**, 729 (1902). Kraus, THIS JOURNAL, **35**, 1732 (1913).

[5a] A very complete review of the literature of the triaryl methyl groups is given by Professor Gomberg in *Chemical Reviews*, **1**, 91–121 (1924).

[6] The property of chaining is much more common than is ordinarily recognized. It is found not only in silicon compounds but also in compounds of boron [Stock, *Ber.*, **56**, 789 (1923); **57**, 562 (1924)], germanium [Dennis, Corey and Moore, THIS JOURNAL, **46**, 657 (1924)] and tin. In the case of the last-named element, chains containing as many as five atoms have been obtained [Greer, *Dissertation*, Clark University, **1924**].

The strongly positive and the strongly negative groups require little discussion, inasmuch as their compounds have properties corresponding precisely to those of compounds of corresponding elements. The strongly positive groups do not form compounds with one another, while the strongly negative groups form compounds of the non-polar type with other strongly negative groups or elements. Compounds between strongly positive and strongly negative groups are true salts, exhibiting electrolytic properties in the pure fused condition as well as in solution.

The compounds of groups occupying an intermediate position in the series of electro-affinities, that is, compounds of the amphoteric groups, are little understood from the physicochemical point of view at the present time and it is these compounds that I wish to discuss more particularly. We have to consider two classes of compounds, namely: compounds of intermediate groups with (1) strongly electropositive elements and (2) strongly electronegative elements. Bearing in mind that these groups are as a rule univalent, their compounds possess particular interest because of the fact that, with the exception of hydrogen, the elements are not capable of forming similar compounds. While other intermediate elements such as lead, tin, antimony, etc., are likewise capable of acting amphoterically, the properties of their compounds differ in marked degree from those of corresponding univalent groups, owing to the higher valence of the elements in question.

As stated, the groups of this type have a constitution corresponding to the formula $R_{n-1}M^n$. Let us consider the compounds of the trimethyltin group, or trimethylstannyl, $(CH_3)_3Sn$, as a typical example. This group in the free state is a non-metallic solid melting at 23°. It exists in solution in the form of a bimolecular compound, $[(CH_3)_3Sn]_2$, which dissociates into the simple group at lower concentration.[7] It reacts readily with both positive and negative elements, thus: $[(CH_3)_3Sn]_2 + 2Na \longrightarrow 2NaSn(CH_3)_3$; $[(CH_3)_3Sn]_2 + Cl_2 \longrightarrow 2(CH_3)_3SnCl$. These reactions correspond to the following reactions of hydrogen: $H_2 + 2Na = 2NaH$; $H_2 + Cl_2 = 2HCl$.

Let us consider, first, the compounds of the trimethylstannyl group with positive elements. These compounds appear to be true salts. They conduct the current, react metathetically with other salts, and in every way behave like true electrolytes. With respect to water, or other acidic substances, these salts are unstable, since they are derivatives of the weak acid trimethylstannane, $(CH_3)_3SnH$. With water, for example, we have the reaction: $(CH_3)_3SnNa + HOH = NaOH + (CH_3)_3SnH$, corresponding to the reaction: $NaH + HOH = NaOH + H-H$.

Trimethylstannane exhibits the properties of a weak acid.[8] For example

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[7] W. V. Sessions, *Dissertation*, Clark University, Feb., **1924**.

[8] Kraus and Greer, This Journal, **44,** 2629 (1922).

with an alkali metal, we have the reaction: $(CH_3)_3SnH + Na = NaSn(CH_3)_3 + \frac{1}{2}H_2$; and with sodium amide: $(CH_3)_3SnH + NaNH_2 = NaSn(CH_3)_3 + NH_3$, $NaNH_2$ acting as base in liquid ammonia solution.

It is evident that the trimethylstannyl group is capable of adding a negative electron to form a stable anion in the presence of electropositive elements or groups. Various carbon groups exhibit a similar behavior. The methyl group belongs to this type. With sodium, methyl forms the compound $NaCH_3$, which is a solid,[9] hydrolyzing in water according to the equation: $NaCH_3 + HOH = NaOH + CH_4$. Methane itself may be considered to be an exceedingly weak acid, although under ordinary conditions this property is not evident. Acetylene, however, has marked acidic properties. That the alkyl groups form anions is indicated by the fact that sodium ethyl, dissolved in zinc ethyl, exhibits electrolytic properties.[10]

If one or more of the hydrogen atoms of the methyl group are substituted by more complex organic groups, such as the phenyl group, the remaining hydrogen atoms become more acidic. On substituting three of the hydrogen atoms of methane by phenyl groups, we have triphenylmethane, $(C_6H_5)_3CH$, a compound which has many properties in common with trimethylstannane. It is somewhat less strongly acidic than the stannane, corresponding to the fact that the free triphenylmethyl group is less electronegative than the trimethylstannyl group.

In liquid ammonia, triphenylmethane reacts with sodium[11] according to the equation: $(C_6H_5)CH + Na = NaC(C_6H_5) + \frac{1}{2}H_2$. Similarly, with sodium amide, we have the reaction: $(C_6H_5)_3CH + NaNH_2 = NaC(C_6H_5)_3 + NH_3$. Triphenylmethane being a weak acid, and sodium amide a weak base, the sodium salt hydrolyzes (ammonolyzes) to a slight extent in liquid ammonia. The corresponding potassium salt is more stable, since potassium amide is a stronger base than sodium amide, while the calcium salt hydrolyzes completely, since calcium amide is a very weak base. With potassium hydroxide[12] we have the reaction: $(C_6H_5)_3CH + KOH = KC(C_6H_5)_3 + H_2O$. This reaction does not go to completion but, by oxidizing the potassium salt as rapidly as it is formed, the triphenylmethane may be oxidized completely to triphenylmethyl peroxide.

It is commonly assumed that hydrogen attached to carbon has no acidic properties. This is not generally true. The acidic properties of hydrogen attached to carbon are ordinarily very weak but, on the introduction of suitable groups, the remaining hydrogen atoms acquire marked acidic properties. The hydrogen derivatives of the hydrocarbon groups which

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[9] Schlenk and Holtz, *Ber.*, **50**, 262 (1917).

[10] *Z. Elektrochem.*, **28**, 469 (1922).

[11] Kraus and Kawamura, THIS JOURNAL, **45**, 2756 (1923).

[12] Raphael Rosen, *Dissertation*, Clark University, Feb., **1923**.

are capable of existing in a free state have measurable acidity. Prevailing views regarding the properties of carbon compounds have been much influenced owing to the conditions under which these compounds have been studied. We usually work with these compounds under conditions of oxidation or weak reduction, in which case the electronegative properties cannot appear. When, however, we study these compounds under conditions of strong reduction, we find that they exhibit a pronounced tendency to act electronegatively.

Let us now consider the properties of the amphoteric groups in the electropositive condition. We may again employ the trimethylstannyl group as a typical example. As already noted, we have the reaction: $[(CH_3)_3Sn]_2 + Cl_2 = 2(CH_3)_3SnCl$. Trimethylstannylchlor ide is a well-known compound which is usually classed with the salts, on the assumption that the trimethylstannyl group acts as a positive ion. When dissolved in water or the alcohols, it is ionized to a marked extent.[13] It may be looked upon as the salt of the base $(CH_3)_3SnOH$. This hydroxide is a very weak base, having a constant, in aqueous solution, of 1.7×10^{-7}, approximately the same as that of aniline.[14]

Is trimethylstannyl chloride a true salt? Since trimethylstannyl is an amphoteric group occupying an intermediate position in the series of electro-affinities, we should not expect its chloride to be a salt. The compounds of corresponding elements are not true salts. We may assume that, if a compound is a true salt, it will be an electrolyte in the pure fused condition. Trimethylstannyl chloride melts at 37° and is not a conductor of the electric current.[15] It is not therefore a true salt. Furthermore, its low melting point and low boiling point (155°) indicate that it should be classed with the non-electrolytes rather than the electrolytes, since these latter compounds have high melting and boiling points.

I have already called attention to the resemblance existing between hydrogen and the trimethylstannyl group. This is further borne out in the case of their compounds with electronegative elements. Hydrogen chloride, HCl, is not an electrolyte. It is a liquid, freezing and boiling at very low temperatures. The liquid is a non-conductor. It is a compound having properties intermediate between those of salts and typical non-polar compounds.

The compounds of the trimethylstannyl group with strongly electronegative elements, then, are non-saltlike substances. Corresponding compounds of other similar groups exhibit corresponding properties. Thus triphenylmethyl chloride is not a conductor in the fused state.[12] Furthermore, the compounds of this type are not only non-conductors in the fused

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[13] Zelinsky and Krapiwin, *Z. physik. Chem.*, **21**, 47 (1896).

[14] Bredig, *ibid.*, **13**, 303 (1894).

[15] Kraus and Callis, THIS JOURNAL, **45**, 2624 (1923).

state but they are also non-conductors in solution in many solvents of high dielectric constant.[15] Thus, trimethylstannyl chloride does not conduct the electric current in nitrobenzene (dielectric constant 36) nor in nitromethane (dielectric constant 39). So, also, triphenylmethyl chloride does not conduct the current in nitrobenzene.

But if compounds of the type of trimethylstannyl chloride are not electrolytes, how shall we account for their electrolytic properties in solution in water and the alcohols? Trimethylstannyl chloride conducts the current readily, not only in the alcohols, but also in ammonia, the primary amines and pyridine. Here, again, let me refer to the analogous compounds of hydrogen. Hydrogen chloride forms electrolytic solutions in precisely the same solvents, namely: water, the alcohols, ammonia and the amines. We have the following reaction which is typical of all acids: $HCl + NH_3 = NH_4Cl$. Hydrogen chloride combines with ammonia to form ammonium chloride, and in ammonium chloride the hydrogen atom of hydrogen chloride, and the hydrogen atoms of ammonia, are associated with a nitrogen atom to form the ammonium ion, which is much more electropositive than is hydrogen itself. May not a similar reaction take place in the case of trimethylstannyl chloride? We have, in fact, the following reaction:[16] $(CH_3)_3SnCl + NH_3 = (CH_3)_3SnNH_3Cl$. Trimethylstannyl ammonium chloride is a stable solid which sublimes at higher temperatures without melting. In its physical properties, it closely resembles ammonium chloride. While trimethylstannyl chloride is soluble in (in fact, miscible with) practically all organic liquids, the ammonia derivative is soluble only in such solvents as ordinarily dissolve salts. Furthermore, solutions of this compound conduct the current. Trimethylstannyl chloride also reacts with pyridine according to the equation: $(CH_3)_3SnCl + C_5H_5N = (CH_3)_3Sn.C_5H_5NCl$. This compound melts at 37° and conducts the electric current. This reaction corresponds precisely with that between pyridine and methyl iodide: $C_5H_5N + CH_3I = CH_3.C_5H_5NI$, in which a methylpyridonium salt is formed. The electrolytic properties of solutions of trimethylstannyl chloride in ammonia and the amines are then to be ascribed to the formation of an ammonium ion in which the trimethylstannyl group is attached to nitrogen in the positive ion.

We may account for the electrolytic properties of solutions of trimethylstannyl halides in aqueous solution by assuming the formation of an oxonium salt. There is this difference between solutions in ammonia and in water: while in solutions in ammonia or the amines we obtain a stable compound in which the stannyl halide is combined with a molecule of the solvent, in water and the alcohols we obtain the original stannyl halide unchanged on evaporating the solvent. Now this property is also char-

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[16] Kraus and Greer, This Journal, **45**, 3078 (1923).

acteristic of the acids. Under ordinary conditions, they do not form stable compounds with water and the alcohols. Yet we have reason for believing that compounds are formed in these solvents in which, at least, one solvent molecule is associated with the hydrogen ion, and it is not improbable that this hydrogen ion is of the oxonium type. It is interesting to note, in this connection, that trimethylstannyl chloride is much less ionized in alcohol solution than are typical salts and that, moreover, its solutions conform to the law of mass action according to conductance measurements. The ionization constant[16] of trimethylstannyl chloride in absolute alcohol at 25° is 0.35×10^{-4}.

We should have a greater degree of confidence in the oxonium theory of the acids if we could obtain stable oxonium salts of simple type. Now, while compounds between hydrogen chloride and ether may be obtained, these compounds are not very stable and their physical properties cannot be studied. It has been found that stable oxonium salts may be obtained in which the hydrogen atoms are substituted by trimethylstannyl groups. If we treat the trimethylstannyl ether, $(CH_3)_3Sn—O—Sn(CH_3)_3$, with the corresponding halide we have the following reaction: $[(CH_3)_3Sn]_2O + (CH_3)_3SnI = [(CH_3)_3Sn]_3OI$. In other words, we have direct combination between the ether and the halide, just as in treating trimethylamine with methyl iodide we have tetramethyl-ammonium iodide formed according to the equation: $(CH_3)_3N + CH_3I = (CH_3)_4NI$. The compounds formed on treating trimethylstannyl ether with trimethylstannyl halides are beautifully lustrous crystals which are stable at ordinary temperatures and for the most part decompose at fairly high temperatures, usually without melting.[17] These compounds are readily soluble in water and the alcohols and form electrolytic solutions. They are much more highly ionized than are the trimethylstannyl halides in the same solvent. By means of silver hydroxide, a strong base is obtained which, according to conductance measurements, is but little weaker than the strongest bases. The chloride conducts the current in the pure fused condition.[18] The fact that oxonium compounds exist, in which three stannyl groups are joined to oxygen, renders it highly probable that in the compounds of the trimethylstannyl halides with ammonia the stannyl group is united to nitrogen. The existence of oxonium compounds of the tertiary type is a further addition to a rapidly growing mass of facts which indicate that the hydrogen ion is, in fact, a complex ion of the oxonium type.

Summary

It is suggested that stable groups of elements may be arranged in a twofold series of electro-affinities similar to that of the elements. It is pointed

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[17] The chloride melts at 93° with slow decomposition.

[18] Observations by T. Harada in the author's Laboratory.

out that the properties of these groups in the free state correspond to those of elements of the same electro-affinity. Groups intermediate in the series exhibit marked amphoteric properties; that is, they appear in an electronegative or electropositive state, depending on conditions.

The properties of the univalent amphoteric groups correspond closely to those of hydrogen, which is the only univalent amphoteric element known. The properties of the trimethylstannyl group and its compounds are discussed in detail and compared with those of hydrogen.

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE STANDARDIZATION OF THIOSULFATE SOLUTION BY THE PERMANGANATE-IODIDE AND DICHROMATE-IODIDE METHODS

BY WILLIAM C. BRAY AND HARRY EAST MILLER

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Vosburgh's recent investigation[1] has probably settled two important problems in volumetric analysis. (1) Potassium dichromate as a standard in iodimetry is accurate within 0.1%, provided the concentrations of acid and iodide are maintained within rather narrow limits during the reaction between dichromate and iodide. The chief sources of error are the slowness of this reaction when the concentrations of acid and iodide are too low, and the liberation of iodine by oxygen when these concentrations are too high. (2) The iodine-thiosulfate titration should always be made in dilute acid, rather than neutral, solution. An explanation of the small error of 0.1 to 0.3% in neutral solution was not given by Vosburgh but is almost certainly the formation of a minute amount of sulfate instead of tetrathionate. That thiosulfate is oxidized completely to sulfate by iodine in alkaline solution, which would correspond to an error of 800% if the product were assumed to be tetrathionate, has been discovered independently by several investigators.[2] If, as seems probable, hypo-iodite and hypo-iodous acid are responsible for this reaction, then the presence of acid eliminates the error by repressing the hydrolysis of iodine.[3]

A third result, given by Vosburgh in the last paragraph of his paper, seemed questionable. He concluded that a permanganate solution, the concentration of which is determined with sodium oxalate by McBride's method,[4] is unreliable as a standard in iodimetry. The error

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[1] Vosburgh, THIS JOURNAL, **44**, 2120 (1922).

[2] Abel, *Z. anorg. Chem.*, **74**, 393 (1912). References to earlier work are given. Compare Bray, Simpson and MacKenzie, THIS JOURNAL, **41**, 1376 (1919), for similar results in Na_2HPO_4 solution.

[3] Bray, THIS JOURNAL, **32**, 932 (1910). Bray and Connolly, *ibid.*, **33**, 1485 (1911).

[4] McBride, *ibid.*, **34**, 415 (1912). See Ref. 11.