FACTORS DETERMINING CHEMICAL STABILITY

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The subject of chemical stability is one of primary concern to chemists, and great progress has been made in recent years in elucidating the factors which determine it. Since but little of the pertinent material has appeared in the English language, and since the significance for chemistry of much that has been done in physics has not been pointed out it has seemed worth while to prepare this review of work already published, and to include in it results of a study of the subject made by the writer during the past two years, in which he has had valuable assistance by Prof. W. C. Bray.

DEFINITION OF STABILITY

The term stability is used by chemists in several senses which it is desirable to distinguish. A substance is usually called unstable if it is hard to keep it from changing into something else. Ferrous hydroxide is unstable in the presence of the oxygen of the air, sodium is unstable in the presence of moisture, and yet each is quite stable by itself. On the other hand hydrogen peroxide, even when protected from external agencies, decomposes at least slowly, and is regarded as unstable. We see here, however, the importance of distinguishing different types of decomposition, for hydrogen peroxide is unstable with respect to water and oxygen, but not with respect to hydrogen and oxygen, as shown by the accompanying changes in free energy:[1] $H_2O_2 = H_2O + \frac{1}{2} O_2$, $\Delta F = -25{,}090$ cals.; $H_2O_2 = H_2 + O_2$, $\Delta F = +31{,}470$ cals. It cannot, therefore, decompose into its elements at ordinary temperatures, and is unstable only because water is more stable.

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[1] Lewis and Randall, Thermodynamics, McGraw Hill Co., 1923.

In nitric oxide we have a substance which may appear quite stable in the sense that it may be kept indefinitely at ordinary temperatures, and yet pure NO could never be formed from its elements at 25° except at the expense of outside energy, for the free energy of the reaction $N_2 + O_2 = 2\ NO$ is 20850 cals.[1]

But even this fact does not mean that the molecule of NO itself is unstable, but merely that the molecules N_2 and O_2 are together more stable, hence the above 20850 cals. do not measure the strength of the bond in the NO molecule, which is a question of primary concern.

Now questions of rate are exceedingly important, but they must not be confused with questions of equilibrium or thermodynamic stability, and in this paper only the latter will be considered. Moreover, we will take care to specify the products of decomposition whenever speaking of the instability of a substance.

The thermodynamic stability of a substance with reference to a specified decomposition is correctly measured by the free energy change accompanying it, but it is unfortunately the case that the free energies of relatively few substances have been determined. We shall have to depend, therefore, chiefly upon the heats of reaction. This can be done without very great danger when comparing reactions of the same type, and for others where the differences are considerable, since the heats and free energies do not often differ by large amounts. When neither of these quantities is known we may often still draw conclusions from the chemical behavior of substances and their methods of preparation.

DISCREPANCIES WITH ELECTROCHEMICAL THEORY

The most valuable guide the chemist has had in dealing with questions of stability is the electrochemical theory first hinted at by Davy and later developed by Berzelius. Although modern discoveries have made it necessary to alter the conceptions of Berzelius, they have given us a theoretical basis still better adapted to the essentials of the Berzelian doctrine. A knowledge of the tendencies of elements to add or give up electrons, as correlated with the Periodic System, and the familiar "replacement series," is still indispensable in the education of the chemist. We apply these ideas not only to determine the relative stability of binary compounds, but also of more complex compounds such as hydroxides, carbonates, double salts, etc., in relation to their dissociation products. Thus, sulfites are more stable than carbonates because, as we say, SO_2 is a more "negative" oxide than CO_2; similarly, $Cu(OH)_2$ gives off water at a lower temperature than $Zn(OH)_2$ because ZnO and H_2O are farther apart, in an electrochemical sense, than are CuO and H_2O.

Difficulties are encountered by the purely electrochemical theory, however, in the realm of organic chemistry, where the assignment of positive and negative valence numbers, or the statement that an electron has left one atom and gone to another, becomes, to say the least, far less reliable as a guide in questions of stability. Even in the realm of inorganic chemistry, when we seek to account for the great stability of molecules like N_2, H_2, and O_2, the simple electrochemical theory becomes almost useless. Considerations of this sort led to the theory of G. N. Lewis[2] that the valence electrons are not the exclusive property of the negative atoms but are shared by both atoms. The remarkable fruitfulness of this theory of the chemical bond, during the brief period since its publication, is well known. It is, however, more a theory of valence and of the nature of the chemical bond than of its strength, and it is evident that the latter topic is one of the utmost importance.

There are, moreover, certain other discrepancies with the electrochemical theory, as ordinarily applied, which appear not to have been discussed, and which serve to make evident some important factors affecting chemical stability. Thus, the nitride of a metal should be more stable the more positive the metal, but lithium nitride is stable whereas cesium nitride is not, although it takes 1.49 volts more to transfer an electron from lithium to nitrogen than from cesium, or 103.1 kg. cals., more per mol of nitride, a very large difference. Magnesium nitride is likewise more stable than barium nitride or sodium nitride, although magnesium is less "positive" than either of the other metals.

[2] G. N. Lewis, This Journal, **38**, 762 (1916); Valence and the Structure of Atoms and Molecules, A. C. S. Monograph, 1923.

Again, it has been shown by Bardwell,[3] in this laboratory, that hydrogen separates at the anode when CaH_2 is electrolyzed, and hence may be regarded as the negative element in the compound. Accordingly, the stability of the hydrides should increase, going from lithium to cesium, and from calcium to sodium, whereas the reverse is true.

With carbides also, although the data are very incomplete, the more stable compounds are apparently formed with the less positive metals higher in the groups, and with the less positive elements, in group 2, rather than those in group 1. In short, if we were making an electrochemical or "replacement" series, using the above compounds as the basis, we would not duplicate the ordinary series obtained by consideration of the more familiar salts of the metals. The fact that the discrepancies obviously are associated in part with low atomic number on the part of both constituents suggested that relative sizes of the component atoms in a compound might prove to be a factor of general importance in determining stability.

TABLE 1

Heats of formation of alkali halides in kilogram calories

	F	Cl	Br	I
Li	120	97	87	71
Na	111	99	90	76
K	109	105	97	85
Rb	108	105	99	88
Cs	107	106	101	90

We have complete data for the heats of formation of the alkali halides, which are certainly near enough to their free energies of formation to indicate their relative stabilities. Table 1 gives values in round numbers in kilogram calories,[4] which show that the fluorides furnish another exception to the usual electrochemical order. It should be noted, further, that although the other three series show the familiar order the rate of change is very dif-

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[3] Bardwell, This Journal, **44**, 2499 (1922).

[4] Cf. Landolt-Börnstein Tabellen.

ferent for the other halides, the chlorides approaching the fluorides.

The smallest alkali metals show a similar preference for oxygen, as shown in table 2, but this becomes negligible with sulfur. Unfortunately, data for the selenides and tellurides are too meager to serve as evidence.

The compounds of the metals of group 2 show similar discrepancies, as shown in table 3, although the maximum stability in the cases where the electrochemical order does not hold is at calcium rather than beryllium, while the chlorides and iodides, on the other hand, increase regularly according to electrochemical theory.

TABLE 2

Heats of formation in kilogram calories

	Li	Na	K	Rb	Cs
Oxides	142	101	87	84	83
Sulfides		90	87	87	87

TABLE 3

Heats of formation of compounds of alkaline earth metals

	F	Cl	I	O	S	Se
Be		113		136		
Mg	209	151	85	144	79	
Ca	239	190	141	152	111	78
Sr	235	196	142	140	110	78
Ba	223	197	148	126	102	70

Facts such as the above, contradicting the simple electrochemical theory so much relied upon by chemists, invite the application of certain recent developments in physics which are of significance in bringing to light various factors which influence chemical stability.

IONIZING POTENTIALS

The basis of the "replacement series" is the ease with which elements lose or gain electrons. As we now usually say, sodium is a very positive metal because it has a loosely held outer electron which readily passes to a chlorine atom, where it is tightly held, completing a stable octet. The resulting positive sodium ion and negative chlorine ion are then held together in the crystal by electrostatic attraction. In potassium the outer or valence electron is more loosely held, so that potassium chloride is formed with greater evolution of energy than is sodium chloride. The ease with which electrons are lost or gained has been measured directly as ionizing potential, or calculated indirectly from spectroscopic data.[5] Table 4 gives values for the metals of groups 1 and 2, which illustrate their harmony with the familiar electrochemical explanations of chemical phenomena, such as are associated with the "replacement series."

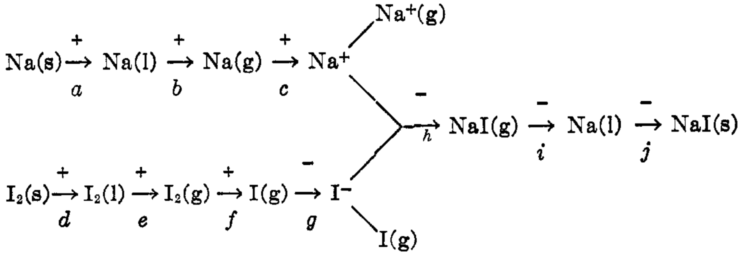
TABLE 4

Ionizing potentials, volts

Li	5.37	Be	>Mg	Be^+	?
Na	5.12	Mg	7.61	Mg^+	14.97
K	4.32	Ca	6.09	Ca^+	11.82
Rb	4.16	Sr	5.67	Sr^+	10.98
Cs	3.88	Ba	5.19	Ba^+	9.96

MELTING AND BOILING POINTS, HEATS OF DISSOCIATION OF ELEMENTARY MOLECULES, ETC.

The ionizing potentials represent the energy involved in removing electrons from gaseous atoms, and hence do not represent all of the energy of formation of a compound like solid NaI from solid sodium and solid iodine. Let us divide this reaction into a series of steps, as has been done by Born[6] and others, as follows:



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[5] See summary by Payne, Proc. Nat. Acad. Sci., **10**, 323 (1924); also Bul. Nat. Res. Council, **9** (1924).

[6] Born, Ber. deut. phys. Ges., **21**, 13, 533, 679 (1919).

The signs indicate the increases and decreases in heat content, ΔH, of the several steps of the process. Since the total ΔH is negative for a stable substance (formed with evolution of heat), the stability will be greater the smaller the (positive) values of steps *a*, *b*, *c*, *d*, *e*, and *f*, and the larger the (negative) values of steps *g*, *h*, *i*, and *j*. Where we do not know the heats of fusion and of vaporization we can use the melting and boiling points to make rough comparisons for different substances between the magnitudes of ΔH for the steps *a*, *b*, *d*, *e*, *i* and *j*. Thus, lithium melts and vaporizes at much higher temperatures than potassium, so that larger values for steps *a* and *b* for lithium tend to make all lithium compounds less stable than the corresponding potassium compounds.

On the other hand, where one compound is less fusible and volatile than another, steps *i* and *j* have larger values and tend to make the former compound more stable. We will return to a consideration of these factors in the later discussion of various examples.

We see that differences in the heat of dissociation of a gaseous molecule into atoms, step *f*, also influences the total heat of the process. Thus the higher stability of Cl_2 as compared to $I_2(g)$ with respect to their atoms tends to reduce the comparative stability of chlorides.

THE SIZE OF ATOMS AND THE ENERGY EVOLVED WHEN COMPOUNDS ARE FORMED FROM GASEOUS IONS

Little attention has been paid until recently to step *h* in the above scheme, the energy involved in the union of the gaseous ions to form the compounds. Born and Landé[7] have published a calculation of the electrostatic potential of the ions in the crystal lattice. They assume that the ions in the lattice are held in equilibrium position by the force of electrostatic attraction, obeying Coulomb's law, balanced by that of repulsion, which varies with the distance *r* by a higher inverse power law. The potential

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[7] Born and Landé, Ber. d. deut. Physik. Ges., **19**, 210 (1918); Born, ibid., **21**, 13 (1919).

energy, u, converted into external energy as N ions of each kind come together is given by the expression:

$$u = N\left(\frac{a}{r} - \frac{b}{r^n}\right)$$

The constant a is 13.94 e^2, where e is the elementary charge, and the value of b is got from the relation that $(du/dr) = 0$ in the quilibrium position. This gives $b = \frac{a r_0^{n-1}}{n}$, where r_0 is the lattice constant. The compressibility depends likewise on du/dr, and in terms of the above assumption is:

$$\beta = \frac{9\, r_0^4}{a(n-1)}$$

The value of n necessary to give agreement with the experimental values is approximately 9 (from 7.75 to 9.6) for the halides of the various alkali metals except lithium, where it is about 5. The lattice constant is related to the density, ρ, and the atomic weights μ^+ and μ^-. For the complete dissociation of the crystal into gaseous ions the heat then becomes $490\left(\frac{\rho}{\mu^+ + \mu^-}\right)^{\frac{1}{3}}$ kgm. cals. for lithium halides and $545\left(\frac{\rho}{\mu^+ + \mu^-}\right)^{\frac{1}{3}}$ for the other alkali halides. The values so calculated by Born are given in table 5.

TABLE 5

Lattice energies from Born and Landé's theory

	F	Cl	Br	I
Li	231	179	167	153
Na	220	182	168	158
K	210	163	155	144
Rb		144	140	138
Cs		156	150	141

It will be noted that the smaller the ions the greater the decrease in potential energy when they unite, and hence the greater the heat of formation from the gaseous ions.

Latimer[8] has criticised the assumption that the field of force about the ions can be calculated on the basis of a rigid structure to the neglect of the changes in potential and kinetic energy of the electrons in each ion. Of course, a purely empirical equation for the potential of the ions in a crystal should, if correct, make possible the calculation of both compressibility and heat of ionization, but the fact that such an equation fits the compressibility data does not make it reliable for calculating heat of ionization because of the wide extrapolation involved. We cannot, therefore, place great reliance in the values in table 5. Nevertheless, there can hardly be any doubt that they are correct in indicating that the heat of ionization increases with decreasing atomic size. Almost any reasonable assumption regarding the laws of force about the ions would give this result, moreover, we know from the ionizing potentials, given in table 4, that the energy require to dissociate an electron increases with decreasing atomic size, and it can hardly be otherwise when a negative ion is substituted for an electron.

The total energy of formation is known, and all of the steps in the process as outlined above except the electron affinity of the halogens, step *g*, and the energy of combination of the gaseous ions, step *h*. The lattice energies could therefore be calculated from thermodynamic data alone if the electron affinities of the halogen atoms were known. Franck[9] has given an interpretation of the spectrum of iodine whereby the electron affinity of the iodine atom is 59.2 kg. cals. Born and Gerlach[10] have pointed out the discrepancy of 21 kg. cals. between this value and the one derived from lattice energies, and concluded that the lattice theory must be altered. More recently, however, Oldenberg[11] has shown this interpretation to be hardly tenable.

Grimm[12] in several comprehensive papers on the Born theory has also attempted to calculate this affinity from the data for the

[8] Latimer, J. Am. Chem. Soc., **45**, 2803 (1923).

[9] Franck, Z. f. Phys., **5**, 428 (1921).

[10] Born and Gerlach, Ibid., **5**, 433 (1921).

[11] Oldenberg, Z. f. Physik., **25**, 136 (1924).

[12] Grimm, Z. f. phys. Chem., **102**, 113, 141 (1922).

formation of the hydrogen halides, assuming that the concordant ionization potentials determined by Foote and Mohler,[13] Knipping,[14] and Mackay[15] represent the splitting of the molecule into hydrogen and halide ions. This, however, is not the case, as Mackay attributed this ionization to the removal of an electron, forming ions of the type HCl^+, and Barker and Duffendack[16] have adduced good evidence in support of this interpretation.

We have, therefore, no sufficient basis for the calculation of lattice energies apart from the somewhat questionable assumptions of Born and Landé. Nevertheless, it can be shown that the lattice energy increases as we go from the larger to the smaller elements, for the difference in lattice constants between the same halide of two alkali metals eliminates the electron affinity of the halogen. This sort of study has been made by Born and his co-workers, and more recently in very thoroughgoing fashion by Grimm.[17] It seems desirable, however, to make a more critical selection of some of the fundamental data used.

For the heats of vaporization of the alkali metals we have fairly concordant values calculated from the vapor pressures for all the metals except lithium.[18] (These do not agree well with the values derived by von Wartenberg and Schultz[19] from a modified Troutons' rule.) I have calculated a value for lithium from my generalization regarding the entropy of vaporization,[20] assuming that the boiling point is 1500°. The alkali metals deviate increasingly from the rule for normal liquids as we descend the group from sodium to cesium, but the deviation with sodium is small, and for lithium is undoubtedly less, so that I have assumed a value between the value calculated from the sodium curve and the one from the curve of a normal liquid.

The values for the heats of fusion are from Landolt-Börnstein

[13] Foote and Mohler, J. Am. Chem. Soc., **42,** 1832 (1920).

[14] Knipping, Z. f. Physik., **7,** 328 (1921).

[15] Mackay, Phil. Mag., **46,** 828 (1923).

[16] Barker and Duffendack, Phys. Rev., **26,** 339 (1925).

[17] Grimm, loc. cit.

[18] Cf. Landolt-Börnstein Tabellen, also Scott, Phil. Mag., **47,** 32 (1924).

[19] von Wartenberg and Schultz, Z. f. Elektrochem., **27,** 568 (1921).

[20] Hildebrand, J. Am. Chem. Soc., **37,** 970 (1915); **40,** 45 (1918).

Tabellen except for lithium, which is obviously much too low, in view of the melting point of the element. Table 6 gives the values used, together with their sums, the heats of sublimation, steps *a* and *b*, in our scheme.

The increase in heat content in kilogram calories when an electron is removed from an atom of alkali metal is got by multiplying the ionizing potentials (table 4) by 23.07, giving for Li, 126; Na, 118; K, 100; Rb, 96; Cs, 90.

The heats of fusion of the alkali halides are known in only four cases, and values for the others have been calculated by assuming constancy of the ratio $\Delta H/T_{m.pt.}$. The error thus introduced into our calculations cannot be very large, for the heat of fusion is but a small part of the whole heat of formation. For the heats of vaporization we have data by von Wartenberg and by Ruff[21] and co-workers. In the few cases where these are discordant Periodic relations have been considered in selecting the more probable value. Table 7 gives the selected values.

TABLE 6

Heats of fusion, vaporization and sublimation of the alkali metals, kilogram calories

	Li	Na	K	Rb	Cs
Heat of fusion	0.8	0.6	0.6	0.5	0.5
Heat of vaporization	42.5	25.4	18.8	18.0	17.6
Heat of sublimation	43.3	26.0	19.4	18.5	18.1

TABLE 7

ΔH for (1) vaporization and (2) fusion for alkali halides

	F		Cl		Br		I	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
Li	54	8	37	5	36	4	37	4
Na	54	8	45	7	40	6	38	6
K	43	7	41	6	39	6	38	6
Rb	40	6	39	6	38	6	37	6
Cs	36	6	37	6	37	6	37	5

From the above data it is possible to calculate ΔH when a gaseous

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[21] Cf. Landolt-Börnstein Tabellen.

alkali ion replaces another from either the gaseous or solid halide. For example, we have:

REACTION	ΔH	CF. TABLE
(1) $Li(s) + NaI(s) = Na(s) + LiI(s)$	+5	1
(2) $Li(g) = Li(s)$	−43	6
(3) $Na(s) = Na(g)$	+26	6
(4) $Li^+(g) + E^- = Li(g)$	−126	4
(5) $Na(g) = Na^+(g) + E^-$	+118	4
Adding		
(6) $Li^+(g) + NaI(s) = Na^+(g) + LiI(s)$	−20	
Further		
(7) $LiI(s) = Li(g)$	+41	7
(8) $NaI(g) = NaI(s)$	−44	7
Adding (6), (7) and (8)		
$Li^+(g) + NaI(g) = Na^+(g) + LiI(g)$	−23	

TABLE 8

−ΔH for replacement of gaseous alkali ions in solid halides by alkali ion of next higher atomic weight

REPLACEMENT	F	Cl	Br	I
Na^+ (g) by Li^+ (g)	29	23	22	20
K^+ (g) by Na^+ (g)	27	19	18	16
Rb^+ (g) by K^+ (g)	5	4	2	1
Cs^+ (g) by Rb^+ (g)	7	5	4	4

TABLE 9

−ΔH for corresponding replacement in gaseous halides

	F	Cl	Br	I
Na^+ by Li^+	25	33	28	23
K^+ by Na^+	15	14	17	16
Rb^+ by K^+	9	2	1	0
Cs^+ by Rb^+	3	3	3	3

Applying this process to the other cases we get the values in table 8 for −ΔH for the replacement of the gaseous alkali ion of one *solid* halide by the gaseous alkali ion of next lower atomic weight, and for the corresponding replacement in the *gaseous* alkali halides we get the values in table 9.

In these tables the effect of different ionizing potentials has been eliminated. It is evident that in all cases the ion of the lighter metal replaces the one of the heavier. This is the reverse of the order shown in the ordinary replacement series where the ionizing potentials obscure the effect of the different attraction between the ions. It will be noted that the change from K to Rb and from Rb to Cs has but little effect but that in going from K to Na the effect is large, and from Na to Li it is still larger. Moreover, the changes in table 8 are largest for the fluorides, diminishing regularly to the iodides, so that we see evidence that the greatest ionic attractions exist not only where the positive ion is smallest, but also with the smallest negative ion, that is, the heat of union is greatest for $Li^+ + F^-$.

It is evident that the affinity of a positive ion for an electron bears some relation to its affinity for a negative ion. Thus the difference in electron affinity between Li^+ and Cs^+ is 36 kgm. cals., while the differences between their affinity for the halide ions, according to the values in table 9, range from 42 to 54 kgm. cals. The same explanation evidently applies in both cases; just as the closer approach of the electron to the smaller ion evolves more energy, so likewise the closer approach of a halide ion to the smaller positive ion evolves more energy. This should be qualitatively true even though the law of force between the ions is quite different from the one assumed by Born and Landé.

This effect of size is very strikingly shown by the large value of ΔH for the replacement of $Li^+(g)$ by $H^+(g)$ in such a reaction as $H^+(g) + LiCl(g) = Li^+(g) + HCl(g)$. Taking the heat of formation of HCl as 22 kgm. cals., the heat of dissociation of H_2 as 84 kgm. cals.,[22] and the ionizing potential of hydrogen atoms as 13.5 volts,[23] and combining with values for Li and LiCl as was done in calculating the figures in table 9, we get the very large value of ΔH for the above reaction of -152 kgm. cals. Therefore $H^+(g)$ easily replaces $Li^+(g)$ from LiCl in spite of the fact that Li metal easily replaces H_2 from HCl.

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[22] Langmuir, J. Am. Chem. Soc., **36**, 1708 (1914); **37**, 417 (1915).

[23] Cf. Bull. Nat. Res. Council, **9**, 112 (1924).

DISTORTION OF THE IONS AS A FACTOR IN THEIR ENERGY OF COMBINATION

Latimer has called attention to the energy involved in the distortion of the ion, and pointed out that this may be different in different combinations. It seems obvious that a given amount of distortion involves less energy change for the outer than for the inner electrons, and this is born out by the fact that the compressibility of the elements in any group of the Periodic System increases with increasing atomic weight. We may conclude from this that the energy of combination of the ions should be more closely related to the *percentage* contraction than to the actual contraction when the ions unite to form the molecule. We have no data upon this, but table 10, showing the percentage contraction upon formation of the solid halides from their *elements*, pointed out by Mr. H. E. Bent, of this laboratory, shows the close connection between this contraction and the heats of formation in table 1. The high value of LiF is particularly striking.

TABLE 10

Percentage contraction upon formation from elements

	F	Cl	Br	I
Li	66	44	34	15
Na	62	44	34	17
K	61	46	38	25
Rb	55	46	39	27
Cs		56*	50*	41*

* Crystal lattice different from the others.

TABLE 11

Differences in 100a for various halides

	F	Cl	Br	I
KX − LiX	132	114	108	106
KX − NaX	71	65	63	60
RbX − KX		25	27	25

Objection may be made that the figures in this table depend upon the values assumed for the individual elements, which vary with temperature. We may avoid any such objection by considering only the distances *a*, between the atomic centers for the salts themselves.[24] Table 11 gives the excess in 100 *a* for the halide of one alkali metal over that of a lighter metal, representing the relative contractions.

It will be seen that a change in the halogen has no effect upon the differences between rubidium salts and potassium salts, but that in going from iodides to fluorides there is a marked contraction for sodium salts as compared with potassium salts, and a still greater relative contraction for lithium salts.

The problem of the relation between chemical stability, contraction upon formation and atomic compressibility has been the subject of extended investigations by T. W. Richards.[25] He has pointed out the different atomic volumes of the same element in the different halides, and has calculated the following internal pressures in kilogram per square centimeter necessary to account for the observed volumes: NaCl, 100,000; NaBr, 85,000; KCl, 65,000; KBr, 54,000. He points out that "as would be expected from the heats of formation, the average internal pressure in the bromides is less than that in the chlorides. On the other hand, the average internal pressure is greater in the sodium salts than in the homologous potassium salts, although the heats of formation show the opposite order." In place of the explanation for this apparent paradox given by Richards, I suggest that this pressure should be related not to total heat of formation, but to the heat of combination of the ions to form the solid indicated in table 8 and confirmed by the contractions in table 11, and in Richard's own values for the atomic volumes in the chlorides and bromides of sodium and potassium.

Turning again to the alkaline earth metals, table 3, we see evidences of the same factors as with the alkali halides. The closeness of approach, in the case of the fluorides and oxides, reverses the electrochemical series for calcium, strontium and barium, but not for beryllium and magnesium. This is probably due to the large difference in the ionizing potentials between

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[24] Cf. The Structure of Crystals, Wyckoff, Am. Chem. Soc. Monograph, Chem. Cat Co., 1924.

[25] T. W. Richards, J. Am. Chem. Soc., **45**, 422 (1923).

magnesium and calcium, seen in table 4, which tends to preserve the electrochemical series.

The fact that the atoms in MgO actually are more distorted than those in CaO, in spite of the smaller heat of formation, is indicated by the figures in table 12 calculated from the densities of the solids. We may, therefore, conclude that the reaction $Mg^{++}(g) + O^{--}(g) = MgO(g)$ would actually give out more energy than the reaction $Ca^{++}(g) + O^{--}(g) = CaO(g)$.

HEAT OF HYDRATION OF GASEOUS IONS

Fajans[26] has discussed the theory of Born and Landé in connection with the heats of hydration of the gaseous ions. When a solid halide is dissolved in a large amount of water the heat of solution is equal to the sum of the heat of ionization into the gaseous ions and the heat of hydration of the gaseous ions. Since the first is known experimentally, if the values of Born are accepted for the second, the third can be calculated. It seems preferable, however, to proceed as in the former case, using thermochemical data only, and calculate the differences in heats of hydration of the gaseous alkali ions.

TABLE 12

	DENSITY		MOLAL VOLUME	Σ ATOMIC VOLUMES*	PER CENT CONTRACTION
	Metal	Oxide			
Mg	1.74	3.65	8.3	25	67
Ca	1.55	3.40	16.5	37	55
Sr	2.58	4.61	22.5	46	51
Ba	3.78	5.72	26 8	48	44

* Taking atomic volume of O = 11.2.

Using the following heats of solution, LiCl, −8.4; NaCl, +1.5; KCl, +4.4; RbCl, +4.7; CsCl, +4.8; and the replacement values in table 8, we have the equations:

		ΔH
	$NaCl(s) + (aq) = Na^{+}(aq) + Cl^{-}(aq).$	1.5
	$KCl(s) + (aq) = K^{+}(aq) + Cl^{-}(aq).$	4.4
Subtracting,	$NaCl(s) + K^{+}(aq) = KCl(s) + Na^{+}(aq).$	−2.9
From table 8,	$KCl(s) + Na^{+}(g) = NaCl(s) + K^{+}(g).$	−19.0
Adding,	$K^{+}(aq) + Na^{+}(g) = K^{+}(g) + Na^{+}(aq).$	−21.9

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[26] Fajans, Ber. d. deut. phys. Ges., pp. 539, 549 (1919).

We see that the heat of hydration of $Na^+(g)$ is 22 kgm. cals. greater than that of $K^+(g)$. By carrying out the same process with all the alkali metals we get the values shown in table 13, with the values of the heats of ionization of the gaseous chlorides from table 9 repeated for comparison.

If the differences in heats of ionization are calculated from the heats of solution of the other halides identical figures with those from the chlorides are obtained.

The table also gives for comparison the corresponding figures for the replacement of $Li^+(g)$ by $H^+(g)$ both in solution and in the gaseous chlorides. The heat of hydration of $H^+(g)$ is seen to be 118 kgm. cals. greater than that of $Li^+(g)$. The smaller the ion the greater the heat evolved in union with water, as well as in union with an electron or with a halide ion. The effect of this is seen in the well known hydration and high solubility of the halides of lithium except the fluorides, where the high affinity seen in table 8 opposes the hydration. Thus, according to our figures, the difference between the compounds of $Li^+(g)$ and $Cs^+(g)$ is 68 kgm. cals. for the fluorides, 64 for the hydrated ions, and 41 for the iodides. Correspondingly, F^- holds Li^+ in preference to water, but I^- does not, so that LiF is insoluble while CsF is very soluble. On the other hand water removes both Cs^+ and Li^+ from I^-, hence both CsI and LiI are quite soluble.

TABLE 13

$-\Delta H$ for differences in heats of hydration of gaseous ions

	REPLACEMENT				
	Li^+ by H^+	Na^+ by Li^+	K^+ by Na^+	Rb^+ by K^+	Cs^+ by Rb^+
In solution	118	33	22	4	5
In gaseous chlorides	152	33	14	2	3

Fajans has given values for the absolute values of the heats of hydration of the ions, but these depend upon the assumption that the absolute electrode potential of the calomel electrode is given by the capillary method, which is only approximately true, and also neglect the fact that electrons in the gaseous state are not the same as electrons in a metal. This error has been pointed out to me by Professor Latimer, who will deal with this phase of the problem in a paper now in preparation. There has also been some confusion in the published work in this field between heats and free energies which must be avoided in the future development.

EFFECT OF VALENCE AND ATOMIC SIZES

In going from an element in group 1 to the one following it in group 2, as from sodium to magnesium, or from potassium to calcium, there is little change in the equivalent heat of formation of the fluoride, but with the oxides there is a marked increase except in the first row. With the nitrides the effect is still more marked, as shown in table 14. Since the elements in group 2 are less positive than those in group 1, this difference is contrary to simple electrochemical theory, and seems rather to be connected with the relative numbers and sizes of the atoms forming the compounds. In Na_3N we have three large atoms surrounding a small central one. Although the bond is doubtless very polar, it is screened by the sodium atoms so that its field cannot operate successfully to build up a stable lattice. The nitrides of the bivalent metals of group 2, however, contain twice as many nitrogen atoms, and the metallic atoms are smaller, so that the screening of the bond by the metallic atoms is impossible, and a stable lat-

TABLE 14

Equivalent heats of formation. Effect of valence

	FLUORIDES	OXIDES	NITRIDES
Li	120	71	16.5
Be	?	68	Stable
Na	111	50	Not stable
Mg	105	72	20
K	109	44	Not stable
Ca	119	76	19
Cs	107	42	Not stable
Ba	111	63	25

tice can be built up. The phosphorous atom, although less negative than the nitrogen atom, is larger, and hence gives more stable compounds with the alkali metals because, presumably, the central atom is less hidden than in the nitrides, and the bond can exert more outside attraction. From the same viewpoint the smallest metal of each group gives the most stable nitride.

The differences between groups 1 and 2 are less for the oxides, because there are fewer screening metallic atoms, although nearly negligible between Li_2O and BeO because of the small size of the lithium atom. The differences practically disappear with the fluorides.

A further effect of size is seen in the increase in the number of oxygen atoms that can be accommodated about the alkali atom as the latter gets larger, leading to the highest and most stable, peroxides being at the bottom of group 1, although the most stable oxide is at the top.

A similar effect of valence is evident in the difference between the stabilities of the oxides and fluorides (or chlorides) of the polyvalent metals. Thus we have V_2O_5, CrO_3 and Mn_2O_7, but the corresponding chlorides and fluorides have never been prepared, in spite of the fact that fluorides are generally more stable than oxides. Likewise we have K_2CrO_4 and $KMnO_4$ but as yet no K_2CrF_8 or $KMnF_8$. In the latter the coördination number would have to be double what it is in the former, due to the difference in valence between oxygen and fluorine, and such a high coördination number as 8 is very rare. We do find it in RuF_8 and OsF_8, where the central atom is larger, just as we have the normal number of 4 exceeded in the case of periodic acid, K_5IO_7, but not with perchloric acid, $HClO_4$. Although iron is a baser metal than ruthenium or osmium, it is too small to show so high a coördination number as 8, so that there is no FeF_8.

INSTABILITY OF UNIVALENT COMPOUNDS OF GROUP 2

It has been difficult or impossible to prepare univalent compounds of the alkaline earth elements.[27] From the standpoint of

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[27] Wöhler and Rodewald, Z. anorg. chem., 61, 54 (1909).

ionizing potentials this has appeared paradoxical, for the electrons do not come off in pairs. The removal of the second electron requires, as shown in table 4, about twice the potential required for the removal of the first electron. Therefore, a bivalent gaseous ion of calcium would remove an electron from a gaseous atom, as shown by the equation: $Ca^{++}(g) + Ca(g) = 2Ca^{+}(g)$, with an energy of 5.73 volts, or 133 kgm. cals. This large energy value, taken by itself, would indicate that univalent compounds should be quite stable with respect to the metal and bivalent compound, whereas, as a matter of fact, the reaction $Ca(l) + 2CaCl_2(l) = 2CaCl(l)$ occurs only with great difficulty at high temperatures, and $CaCl(s)$ is unstable at lower temperatures. The explanation of this apparent paradox seems to lie, at least partly, in the large energy previously shown to be involved in the combination of ions. This energy is evidently greater than the energy involved in the removal or addition of electrons. If we make the plausible assumption that this would hold true in group 2 also, then, since ΔH for the reaction $Ca^{++}(g) + E^{-} = Ca^{+}(g)$ is -273 kgm. cals.; ΔH for the reaction $Ca^{++}(g) + Cl^{-}(g) = CaCl^{+}(g)$ should be still larger, say $-(273 + x)$ cals.; also since ΔH for $Ca^{+}(g) + E^{-} = Ca(g)$ is -140 cals., ΔH for $Ca^{+}(g) + Cl^{-}(g) = CaCl(g)$ should be larger, $-(140 + y)$, and likewise for $CaCl^{+}(g) + Cl^{-}(g) = CaCl_2(g)$, say $-(140 + z)$, but y and z should both be made much less than x. By combination of the above equations we get ΔH for the reaction $2CaCl(g) = Ca(g) + CaCl_2(g)$ to be $-(x + z - 2y)$ which will be negative, and hence the CaCl relatively unstable, if $(x + z) > 2y$, which might easily be the case if our assumptions are true regarding the relative magnitudes of x, y and z. The corresponding reaction between solids, of course, introduces other factors, but the above discussion at least shows that the great stability of $2Ca^{+}(g)$ with respect to $Ca(g) + Ca^{++}(g)$ does not necessarily require that $2CaCl(s)$ should be stable with respect to $Ca(s) + CaCl_2(s)$. This explanation avoids the necessity of making the assumption, contrary to the ionizing potentials, of any pairing of the electrons in the calcium atom, although not denying its possibility in the halide molecules.[28] It is interesting to observe that CaCl would be what G. N. Lewis has called an "odd molecule," having an odd number of electrons. Such molecules have but a rare existence, tending to pair unless oxidized or reduced. We see this pairing in the case of mercurous ion, Hg_2^{++}, which is thus rendered capable of stable existence. We might expect some tendency to pairing in CaCl, which may cause it to assume some other than the sodium chloride lattice. The fact that it is colored is significant.

Other cases where a lower compound is stable with respect to higher compound and metal, as $FeCl_2$ with respect to Fe and $FeCl_3$, are mostly cases where the atom has a variable kernel. Lack of the required data makes their discussion at this time premature.

TABLE 15

	MgF_2	CaF_2	BaF_2	PbF_2	$PbCl_2$	$PbBr_2$	ZnS	CdS	HgS
m.pt.	910	1360	1280	840	500	380	1850	1750	1450
$-\Delta H$	209	239	223	108	86	64	43	34	11

MISCELLANEOUS EXAMPLES

In addition to the numerous cases discussed in the foregoing paragraphs, several others may be cited that serve to illustrate well certain of the factors involved in stability. We have seen that the energy with which gaseous ions are attracted to each other is a factor of fundamental importance. Now the same forces responsible for this are in general responsible for building up a stable crystal lattice, one which resists melting and vaporization. We may note a certain parallelism between the lattice energies of the alkali halides, table 9, and their melting and boiling points.

Dr. W. Westwater has traced this connection for a large number of substances. Table 15 gives a few examples. It is noteworthy

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[28] G. N. Lewis, Valence and the Structure of Atoms and Molecules, Chem. Cat Co., 1923, p. 61.

that one of our best refractories, ThO_2, has both the highest heat of formation and the highest melting point of the Group 4 oxides.

A particularly striking case of the stabilizing effect of large crystal forces is seen in comparing CO_2 and SiO_2. We may assume that the small size of the carbon atom favors the stability of the former, while the more electropositive character of silicon favors the latter. In order to eliminate these effects so far as possible, we give, in table 16, the ratio of the equivalent heats of formation of oxides to chlorides for these elements and the six preceding. We see that the stability of the oxide as compared with the chloride is *greater* for Li, Be and B, than for Na, Mg and Al, respectively, but that it is *less* for C than for Si. We may assume that for SiO_2 *gas* the figure would be about 1 instead of 1.53, and that the excess of the latter is to be attributed to the large heat of sublimation of solid SiO_2.

TABLE 16

Li	0.73	Be	1.34	B	1.51	C	1.26
Na	0.51	Mg	0.95	Al	1.17	Si	1.53
Ratio	1.43		1.41		1.29		0.82

We may expect, similarly, a large heat of formation of SnF_4 compared with $SnCl_4$, because the former is a solid with a high melting point, while the latter is a volatile liquid. This heat has never been measured, but since ΔH for SiF_4 is nearly twice ΔH for $SiCl_4$, we may expect that ΔH for SnF_4 would be *more* than twice as great as ΔH for $SnCl_4$ (140) or more than 280 cals.

We may recall here the relatively high stability of the hydride and carbide of lithium, mentioned in the opening paragraphs, and note that this is susceptible to the same explanation as has already been given for the compounds with the other elements with small kernels. It is interesting to find that just as oxygen tends to give stable peroxides with large atoms, on account, apparently, of the disparity in atomic volume, so carbon tends to give acetylides in groups 1 and 2 rather than simple carbides. It is the carbide of the smallest element only in group 2, Be_4C_3, that gives methane with water rather than acetylene.

The increasing stability in going from HI to HF is not surprising in the light of ordinary electrochemical considerations, but even here we can see the effect of the small size of the hydrogen and fluorine atoms when we note that the difference in $-\Delta H$ between HF and HI is 32 kgm. cals., while between CsF and CsI it is only 17 kgm. cals. This same factor doubtless gives H_2O and exceptionally high stability compared with H_2S ($-\Delta H$ for the gases, 58.3 and 2.7 respectively) and NH_3 likewise with respect to PH_3. There is no such difference between Na_2O and Na_2S, between Ag_2O and Ag_2S, and Cs_2S is even more stable than Cs_2O (cf. table 2).

The preference of atoms of small size for each other, evident throughout this paper, may be cited in explanation of the fact that the chemistry of carbon is chiefly an account of its combinations with hydrogen, nitrogen and oxygen, elements with small atomic kernels.

The material in this paper should serve to emphasize the importance of a determination of one of the two unknown quantities still remaining in the steps into which the formation of a compound has been divided, viz., the electron affinity of the halogen atoms or the energy of combination of the gaseous ions. The most promising attack upon the latter problem seems to be offered through the study of band spectra.