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ATTEMPT TO SEPARATE THE ISOTOPIC FORMS OF LEAD BY FRACTIONAL CRYSTALLIZATION.

BY THEODORE W. RICHARDS AND NORRIS F. HALL.

Received January 29, 1917.

Although the complete inseparability of isotopes by chemical means has been frequently asserted, the evidence on which this assertion is based has always seemed insufficient. The methods used have been fractional crystallization and precipitation, but these processes have seldom been carried out more than ten times in a particular case, and frequently six or seven crystallizations have been thought a sufficiently thorough test of inseparability. A search of the literature revealed only one investigation, that of Radiothorium and Thorium by McCoy and Ross,[1] where as many as one hundred repetitions of a given process had been made. Thorium nitrate was dissolved in nitric acid and reprecipitated one hundred times with excess of ammonia, but without change in the relative concentration of the isotopes. Precipitation with hydrogen peroxide (forty times) was also without result.

It seemed worth while, therefore, to apply to the important generalization of Fajans, Russell, Fleck and Soddy a more searching test carrying the fractionation further, and using as a criterion of success not only

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[1] THIS JOURNAL, 29, 1709 (1907).

the measurement of radioactivity but also the determination of atomic weight.

The lead from Australian carnotite, with which the kindness of Mr. S. Radcliff and Mr. E. R. Bubb had supplied us, and which had been used in previous atomic weight and density determinations in this laboratory,[1] seemed well suited to our purpose, since its low atomic weight indicated a composition of three or four parts of the isotope (usually assumed to be radium G) to one of lead; and its β-ray activity showed that it contained sufficient radium D to serve as a basis for ionization tests of the possible separation of this isotope from the inactive varieties. The excellent work on radium D and lead by Paneth and von Hevesy[2] had shown indeed that no one of the many and diverse chemical methods applied by them had effected any separation of these substances, but even here no single operation had been repeated often enough to detect the effect of exceedingly small differences in chemical or physical properties.

Preliminary Preparation of Material.

About one kilogram of the radioactive lead was taken for this work. This included much of the purified samples A, B and C of the atomic weight work already referred to, some of which had not been used, and some of which had been recovered from the completed analyses. The samples of metallic lead which had been used in spectrographic tests and density determinations were also added, as well as all the mother liquors remaining from the preparation of the purified samples. Much of this material was already in the form of nitrate, some in the form of chloride and some was metallic. The chlorides were converted into nitrates by repeated evaporation with pure nitric acid, and the metal was dissolved in the same acid. All the nitrates were then combined, dissolved in the least possible quantity of boiling water, and precipitated by the addition of large quantities of pure concentrated nitric acid and cooling in an ice bath. The crystals were separated from the mother liquor with a porcelain funnel, washed with concentrated nitric acid, and the washings and mother liquor united. The strongly acid mother liquors were evaporated to fuming with sulfuric acid, and the sulfates almost completely precipitated by dilution. The sulfates were converted to carbonates by boiling with sodium carbonate, washed nearly free from sodium and dissolved in nitric acid. The small amount of nitrates thus obtained was evaporated to dryness and added to the bulk of the nitrates. No attempt was made to purify farther at this stage, because the unavoidable introduction of much silica during the fractionation (as well as possible accidental contamination) made necessary the thorough purification to which the samples were subjected just before the final tests.

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[1] Richards and Wadsworth, THIS JOURNAL, 38, 1659 (1916).

[2] *Sitz. d. k. Akad. Wiss., Wien*, 122, IIa, 993 (1913).

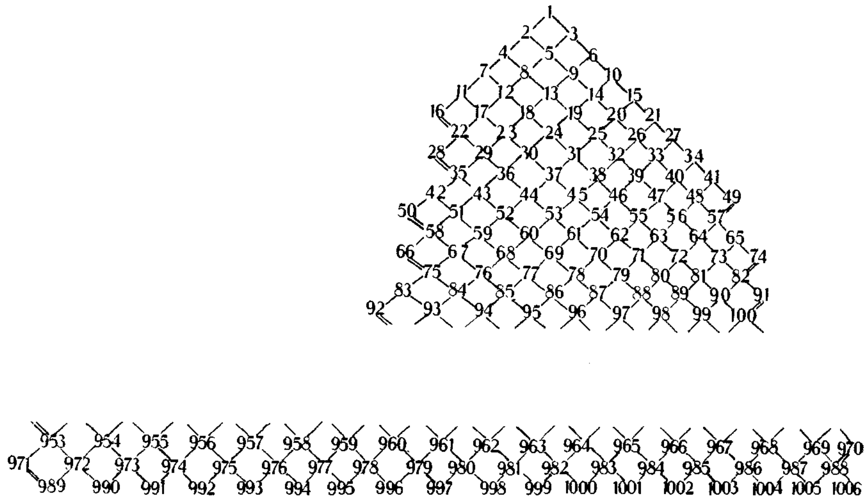
Fractional Crystallization.

The method of crystallizing the nitrate by cooling the boiling nearly saturated aqueous solution was adopted after preliminary experiments on the chlorate and perchlorate of lead had indicated the superiority of the nitrate to these more soluble salts for the work in hand.

This superiority consists in the well-known habit of the nitrate of forming compact, large prisms on crystallization from water solution, which can be very completely freed from mother liquor merely by drainage, as well as in its slight tendency to supersaturation, and the consequent rapidity with which crystal-liquid equilibrium is attained.

The whole of the nitrate was then dissolved in distilled water and evaporated until a crust began to form. This was called Fraction 1. After cooling to room temperature the mother liquor was poured off and formed Fraction 2. To the crystals from Fraction 1 was added sufficient water to dissolve them, and the solution was called Fraction 3.

Fractions 2 and 3 were evaporated to saturation and cooled as Fraction 1 had been, the liquor from 2 forming Fraction 4. Fraction 5 was made by adding the liquor from 3 to the crystals from 2, and water was added to the crystals from 2 to form Fraction 6. This process was continued as shown in the diagram until, as occurred first with Fraction 16, one of the end fractions became too small to work with conveniently and was consequently added entire to the mother liquor from Fraction 17 to form Fraction 22. This expedient was resorted to wherever the end fractions



Scheme of fractional crystallizations. The upper part of the diagram depicts the arrangement of the first 100 crystallizations. It contained 16 tiers of fractions. 56 tiers of fractions, including 853 crystallizations, are omitted from lack of space. The last three tiers are given at the bottom of the diagram.

became inconveniently small. In all, seventy-five courses or tiers of fractions were obtained, most of the last of which contained eighteen fractions to a tier. The number of the last fraction was 1006.

The crystallization was carried out entirely in porcelain, at first in large evaporating dishes, then, as the fractions became smaller, in casseroles covered with watch glasses. The hot casseroles were usually set in evaporating dishes full of cold water, which was frequently changed to hasten cooling. The fractionation was stopped after about a thousand repetitions because, since an accuracy of 2% was hoped for in the final tests, a thousand fractionations would show whether a difference in solubility amounting to one part in fifty thousand for a single crystallization existed or not. In other words, if the end fractions tested at this point showed no difference in the relative concentrations of their components, within the expected error of measurement of 2% we should have proof that no complete separation could be attained by this method in less than *fifty thousand fractionations.*

Through the courtesy of Professor Gregory P. Baxter, the facilities of the T. Jefferson Coolidge Memorial Laboratory were extended to one of us during the summer of 1916, when this part of the work was carried out. Thanks are due to Professor Baxter, not only for this kindness but also for many helpful suggestions which his experience with rare-earth separations made doubly valuable.

Repeatedly the advantage of centrifugal separation of mother liquor from crystals has been demonstrated in cases of ordinary crystallization where the crystals and mother liquor are very different in composition. It is possible to show, mathematically, however, that where there is no such great difference the advantage of centrifugal draining is very much less, and in the present case it was found by this calculation that the gain in effectiveness of separation was less than the disadvantage caused by the increased time necessary for the centrifugal treatment of the thousand precipitates. Making the reasonable assumption that the difference in solubility in this case is probably not greater than 2×10^{-5}, the relative advantage of centrifugal over gravitational drainage is seen to be certainly not greater than 1.5 : 1, so that it would be hopeless to try to increase the rapidity of separation by this means. Even under the best conditions with multiple-basket power centrifugals which could be stopped almost instantly, the time required would certainly be more than half again as much as for mere gravitational drainage. Therefore, in the present case centrifugal draining was not adopted. Baxter, in his crystallizations of praseodymium and neodymium compounds, had come to the same conclusion from practical experience. A note discussing this matter mathematically will soon be published by one of us.

Purification.

Because of the smallness of the end fractions, it was necessary to unite several to obtain a sufficient quantity of material for purification.[1]

From the mother liquor, or "more soluble" end, Fractions 989–992 were taken, united, and called Sample A. Sample B was made up of Fractions 999–1006 from the crystal, or "less soluble" end. From this point on, the two samples were treated in an identical manner. Chiefly to remove the large amount of silica which had dissolved from the casseroles during the fractionation, the crystals were first electrolyzed in warm concentrated solution between platinum wires. The well-formed flat leaflets of lead were removed from time to time, with a glass rod, rinsed with a stream from a wash bottle, and preserved in quartz dishes until all the metal had been deposited from the solution. The crystals were further washed from time to time, and all washings returned to the electrolysis bath, which was gradually reduced in volume as the concentration of lead became smaller. The lead crystals were then dissolved in a nitric acid made by diluting with the purest three times distilled water, nitric acid which had itself been distilled through a platinum condenser with rejection of the first third. The excess of acid was evaporated, and the crystals of lead nitrate dissolved in the purest water, filtered through a platinum Gooch crucible, and precipitated by the addition of a large excess of redistilled nitric acid and cooling with ice. The crystal meal thus obtained was freed from adhering acid in the platinum centrifuge, washed centrifugally with purest concentrated acid and redissolved in the least possible amount of pure boiling water.

Five precipitations with centrifugal drying were made in this way. The crystals from the fifth crystallization were placed in a quartz dish and dissolved. From this solution lead chloride was precipitated by passing in pure hydrochloric acid gas made by warming the purest acid of commerce. The chloride thus obtained was dried in the centrifuge, washed with cold water, and redissolved in boiling water. Four crystallizations as chloride followed. A little hydrochloric acid was added to the solution each time to prevent the formation of basic salt and to render the chloride less soluble. The last crystals, after centrifugal washing and drying, were preserved in an exhausted desiccator over fused potash. Nothing but platinum and quartz vessels were used.

[1] This action nullified the effect of 19 crystallizations on the more soluble end and 83 crystallizations on the less soluble end. Thus the total number of effective crystallizations was 904. The mother liquor on the less soluble end resulted from an average of 71 tiers of successive products and on the more soluble end from an average of 65 tiers. It is to be regretted that this reduction in the efficiency of the process was rendered necessary by the small yields at the two ends of the line, but enough crystallizations remained effective to test the question at issue, at least in a preliminary way.

The Determination of Atomic Weight.

For these determinations the usual procedure was employed. About 5 g. of the dried crystals were placed in a platinum boat, which with its container had been carefully weighed. The boat was gradually heated in a quartz tube attached to the usual "bottling apparatus," in a current of pure dry hydrochloric acid gas. After nearly all the residual water had been driven from the crystals, the temperature was raised so as to fuse the salt, which was then cooled as quickly as possible in a current of pure dry nitrogen prepared by the Wanklyn process.

Mayer[1] has shown that against an excess of pressure (such as was always maintained within our tube) no oxygen diffuses through a layer of quartz even as thin as 0.5 mm.; and our tube walls were 2.5 mm. thick. This observation is confirmed by our experience. The hydrochloric acid delivered from the end of the tube dissolves in water without visible residue (indicating the absence of more than a trace of any slightly soluble gaseous impurity) and very rarely was there any significant corrosion of the boat, which would have occurred with only a trace of oxygen. Only once when the salt was kept fused a long time, its brownish color on cooling showed that a little platinum had dissolved. This sample was, of course, rejected. The delicacy of this color test is shown by the weights of the boat before and after this fusion which differed only by 0.24 mg., although the salt was distinctly brown. No trace of color was observed in any other case, nor was the loss of weight of the boat otherwise over 0.09 mg.

After the salt had cooled, and the nitrogen had been replaced by dry air, the boat was pushed into the weighing tube, bottled, and reweighed.

The boat and salt were next heated at 80–90° on an electric stove in a glass flask containing about a liter of water to which enough pure nitric acid had been added to prevent the formation of basic salt, until the lead chloride had all dissolved. One sample boiled for a few minutes and was rejected at once for fear that a trace of the salt had been carried out by spray. As usual,[2] a small amount of siliceous and carbonaceous residue had to be removed by scrupulously quantitative filtration through a tared Gooch-Monroe crucible. On the average, about twice as much was found in the more soluble fraction as in the other. The weight thus removed was subtracted from the weight of the fused salt. Before filtration the boat had been carefully lifted out and thoroughly washed, and the filtrate was collected in the precipitating flask.

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[1] E. C. Mayer, *Phys. Review*, 6, 288 (1915) bottom of page. Incidentally it may be noted that Mayer's interesting results seem to indicate that when diffusion takes place it is rather of the nature of transpiration through actual holes than solid solution—for in the latter case small difference of pressure would make far less difference than he observed.

[2] Richards and Wadsworth, THIS JOURNAL, 38, 2616 (1916).

A supposedly equivalent weight of silver was next dissolved in pure nitric acid mixed with an equal bulk of water in a flask with a chain of bulbs ground into the neck, a steam bath being used to heat the solution. More water was then added and the temperature raised until a few seconds' gentle boiling had removed nitrous fumes. The solution having been made up to a liter, it was added very slowly with constant agitation to the lead chloride solution. Actinic light was henceforth rigorously excluded from the precipitated silver chloride. The precipitate was coagulated by violent shaking, usually for fifteen minutes, and allowed to stand at least twenty-four hours, with further occasional shakings, before samples were removed for tests. The end point was found by the customary method by means of the nephelometer, and tested for several days to be certain that it did not change.

Vacuum corrections were applied as usual, and all customary precautions were taken.

Previous to this work, two analyses of ordinary lead had been made.[1]

TABLE I.

Analysis.	Sample.	$PbCl_2$ corr. to vacuum.	Ag corr. to vacuum.	Ratio $PbCl_2 : 2Ag$.	At. wt. Pb.
		The Atomic Weight of Ordinary Lead.			
1	Pb	7.13723	5.53723	1.28895	207.187
2	Pb	7.60063	5.89675	1.28895	207.186
				Av.,	207.187
		Atomic Weight of End Fractions of Isotopic Lead.			
7	A	3.70016	2.87854	1.28543	206.426
9	A	4.79633	3.73154	1.28535	206.409
14	A	4.64577	3.61412	1.28545	206.431
				Av.,	206.422
10	B	4.64736	3.61568	1.28534	206.406
11	B	4.87838	3.79519	1.28541	206.422
15	B	4.68396	3.64425	1.28530	206.399
				Av.,	206.409

Ag = 107.880 Cl = 35.459

This table includes all the analyses of the materials which were completed; any which had become the object of suspicion were rejected at an early stage.

Obviously, if the fractional crystallizations produced any change in the relative concentrations of radium G and lead, this change is very small. The means of the two series of determinations of isotopic lead differ only by about 6 parts in 100,000. This is certainly within the bounds of possible experimental error, though the low "average errors" of the two sets

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[1] The fused chloride made from this lead contained no perceptible trace of insoluble residue.

(0.008 unit in each case) tempt one to assign a meaning to the observed difference. At any rate, we are safe in concluding that assuming the atomic weights of radium G and lead to be 206.0 and 207.2, respectively, no change in concentration greater than 13/1200 or 1.1% has been obtained by nine hundred crystallizations. Even supposing that a real difference in solubility exists, and making the further conservative assumption that the bunching of the end fractions reduced the effect of the crystallization by one-fifth, it is evident that complete separation could not be attained in less than seventy thousand fractionations. It is interesting to note again that the average amount of residue in the "more soluble" Fraction B, which must have contained a far larger original siliceous impurity, was 2.3 times as large as that in the "less soluble" Fraction A, and B is also the one which shows the lower atomic weight. This is confirmatory of the experience of Richards and Wadsworth, who say[1] "It is noticeable that in general those preparations which contained appreciable amounts of the residue were slightly lower than the others as regards the final atomic weight obtained." Perhaps a trace of basic salt is carried away with the residue, thus causing its actual weight to be too great; and because the actual weight is subtracted from the total lead chloride, the apparent atomic weight of lead would consequently be too low. In that case the slight difference between Series A and B might be attributed to experimental error from this cause. The matter will receive further attention; in any case it does not seriously affect the conclusion.

Estimation of Radioactivity.

The β-ray activity of the lead used indicates that it contains, in about 3 parts so-called "radium G" and 1 part lead, an amount of "radium D" of the order of 10^{-7} parts. This is betrayed by the steady growth of a penetrating β-ray product ("RaE") which comes to practical equilibrium with its parent in about a month after they are separated. Evidently the ionization, if the α-rays from the polonium present are cut off, caused by a weighed amount of the material under constant conditions, is a measure of the concentration of radium D relative to its isotopes "radium G" and lead. Thus the determination of the activity of the end fractions gives information as to the relation between the solubility of the nitrate of radium D and the mean solubility of the nitrates of radium G and ordinary lead, a relation of great interest because it cannot be tested by atomic weight determinations, and because the difference between the theoretical atomic weight of radium D and that found for the mixture is $210 - 206.4 = 3.6$, or three times as large as that between radium G and lead. Any difference in the properties of isotopes might naturally be expected to be greater, the greater the difference between the atomic

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[1] *Loc. cit.*, p. 2616.

weights; hence this case should afford an especially favorable test of the theory of complete identity.

The method was as follows: To eliminate differences in moisture-content, and consequently in absorptive power, the two samples were kept in the same exhausted desiccator after purification. When 66 days had elapsed 10.25 ± 0.03 g. of each sample were weighed into a marked metal dish and tamped with a platinum spatula. The material formed a layer of thickness defined by the expression 0.88 g./cm^2. This is far too thin to give a maximum ionization due to the complete absorption of the β-rays from the lowest layers, but is thick enough so that no great accidental changes in thickness needed to be feared, and the effect of small changes was annulled as described below. The dishes were covered in turn with the same thin sheet of paper and introduced into a grounded aluminum-leaf electroscope which was very kindly loaned by Professor William Duane. The rate of fall of the leaf was then observed with a stop-watch in the usual manner. The position of maximum sensitiveness was ascertained by preliminary experiments, and the telescope adjusted to this position. The leaf was then always charged to such a potential that it was at the same division of the scale at the beginning of each measurement. The time taken for it to reach another division on the scale (always the same one) was then noted. By this means all errors arising from differences of potential, differences of stiffness of the leaf in different positions, and inhomogeneity of the scale were at once eliminated. The leaf was charged first to an indefinite potential higher than that desired, then by means of an active preparation of polonium held near the base of the electroscope, it was quickly discharged to a point a few scale divisions above the initial mark, and its slow passage across this mark was then observed at leisure. The two dishes were introduced alternately into the electroscope to eliminate the effect of changes in the natural leak, and were thoroughly stirred and repacked between every two measurements to allow for small accidental differences in thickness. The dish not in use was removed always to the same position at a distance from the electroscope and heavily screened, so that no variation in the amount of radiation from this source could affect the rate of fall. The electroscope was carefully screened from all other radioactive material and from neighboring sources of X-rays. Illumination was secured from a tungsten filament lamp at a considerable distance from the leaf, and any convection currents caused in the gas inside the electroscope-case by radiation from this source must certainly have reached a steady state before the work was begun.

These somewhat elaborate precautions are discussed in detail, because it was not until many preliminary experiments had shown the necessity of observing them, that a satisfactory degree of reproducibility was obtained. Thanks are due to Drs. David L. Webster and Harry Clark for much kindly suggestion and assistance.

It is believed that the table below, which includes all the observations affected by no known source of error, represents about as good reproducibility as this electroscope can be made to give. The chief difficulty is in focussing so sharply on the edge of the leaf that the precise instant of its passage of any scale division can be exactly estimated.

TABLE II.

											Average.
Sample A.	11.30	11.43	11.69	11.56	11.61	11.47	11.49	11.50	11.41	11.58;	11.504
Sample B.	11.32	11.62	12.06	11.43	11.70	11.34	11.32	11.43	11.47	11.36;	11.505

The ionization is expressed in arbitrary units (scale divisions per minute). The natural leak (which must have been the same for both as they were taken alternately) was found to be 0.50 ± 0.01. The agreement of the means to one part in ten thousand must be regarded as fortuitous, since their mean probable error is about 0.11 unit. This error, divided by the mean value from which has been subtracted the natural leak, is a measure of the accuracy of the determination. Its value is $\frac{11}{1150-50} = \frac{1}{100}$. This work definitely shows, then, that no change in the relative concentration of radium D and its isotopes as great as 1% has occurred in nine hundred fractionations, and certainly gives no indication that even a smaller change has occurred. In other words, making the same conservative assumption as before, we have proof here that *radium D* cannot be completely separated from its isotopes by this method in less than *eighty thousand crystallizations*.

If ordinary lead is a mixture of isotopes, this mixture must have been made very long ago while the earth was still in a highly mobile condition (since all the ordinary lead throughout the world seems to have the same atomic weight[1]). Could the composite nature of ordinary lead be proved, the identity of the several samples through geological aeons would form another argument in favor of the inseparability of the constituents.

To the Carnegie Institution of Washington we are greatly indebted for some of the apparatus and material used in this research, which is to be continued in the near future.

Summary.

Lead from Australian carnotite (believed to contain about one part of ordinary lead to three parts of radium G, with a mere trace of radium B) has been fractionally crystallized over one thousand times as nitrate, and the end-fractions purified.

The atomic weights of the samples so obtained from the crystal and the

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[1] Baxter and Grover, THIS JOURNAL, 37, 1058 (1915).

mother liquor ends of the series, respectively, agreed within the experimental error of 6 parts in one hundred thousand.

The β-ray activities agreed within the experimental error of 1%.

These observations indicate that the nitrates of radium D and lead on the one hand and radium B and lead on the other hand could hardly be separated, if at all, by less than 100,000 crystallizations.

Hence one might infer that the molal solubilities of the nitrates are probably essentially identical. The outcome gives strong experimental support for the hypothesis that isotopes are really inseparable by any such process as crystallization.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE ORIENTATION OF MOLECULES IN THE SURFACES OF LIQUIDS, THE ENERGY RELATIONS AT SURFACES, SOLUBILITY, ADSORPTION, EMULSIFICATION, MOLECULAR ASSOCIATION, AND THE EFFECT OF ACIDS AND BASES ON INTERFACIAL TENSION.[1]

(SURFACE ENERGY VI.)

BY WILLIAM D. HARKINS, EARL C. H. DAVIES AND GEORGE L. CLARK.[2]

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Introduction: Double Electrical Layers.

The investigations presented in this paper were started as a study of the effect of chemical constitution upon the energy relations at the surface of a single liquid, and at the interface between two liquids and were sug-

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[1] This paper is a direct continuation of a paper in the March (1917) JOURNAL on "The Structure of the Surfaces of Liquids, and Solubility as Related to the Work Done by the Attraction of Two Liquid Surfaces as They Approach Each Other."

[2] A part of the work in this paper was done by Harkins in 1909 in the Institut für physikalische Chemie and Electrochemie in Karlsruhe, at the suggestion of Professor Fritz Haber, and we are indebted to him for the suggestion that we continue the work in this country. Parts of the paper were presented at the Boston meeting of thel Socety in 1909, and at the New Orleans meeting. Another part was prepared in abstiract for presentation at the Symposium on Colloids held by the American Chemica Society in September, but was not accepted. An abstract of a paper presented at this Symposium by Irving Langmuir gives somewhat similar views to some of those developed by us, and for this reason it has been thought best to publish at once the data we have collected. Our accumulation of data has been greatly delayed by the fact that the correction curve is still incomplete, though work was begun upon it in this laboratory four years ago, and we have wished to hold our other results until they can be made as accurate as possible. The curve is almost complete, and our further results upon this subject will soon be ready for publication. The work of Langmuir and that which we present in this paper, while developed independently from somewhat different starting points, are alike in that we have both developed *the same fundamental idea: that surface tension phenomena in general are dependent upon the orientation and packing of molecules in surface layers, and that the forces involved in this action are related to those involved in solution and adsorption.* Our interest in this subject originated