temperature, chiefly by reason of the dominant influence of a small and changing denominator.

For anhydrous salts, since $c = 0$, a low value of $x - c$ means simply a high molal solubility. For potassium nitrate, the values of x at 10 and 50° are 26.7 and 6.6, respectively, and curvature is not yet evident. For ammonium nitrate, the values of x at 50 and 100° are 1.3 and 0.42, respectively, and curvature is marked. Marked curvature is likewise shown by silver nitrate (graph X), and would inevitably be shown by such salts as potassium thiocyanate,[16] whose saturated solutions reach a mole fraction of salt equal to unity, were the pressure data for these available.

In the case of salts forming hydrated solid phases, it is the solubility as stated in terms of moles of hydrate that is significant. This must obviously have large and quickly changing values near a congruent melting point, for there the solubility becomes infinite; while simultaneously $x - c$ is approaching and finally attaining the value zero. In Fig. 2, the maxima shown on graphs III, V, VII, XI, XII and XIII are each not far removed in temperature from a congruent melting point. The values of $x - c$ at these maxima are about 1.5, 1.0, 0.8, 0.24, 0.36 and 1.3, respectively.

Derby and Yngve[13] in discussing the decrement of aqueous vapor pressure with increasing temperature in the case of saturated solutions of magnesium chloride hexahydrate stated that this was "due to the large increase in solubility of the hydrate near its transition temperature." Rather the criterion for large increase in solubility is proximity to the congruent melting point, which in this instance is close at hand although "concealed." In numerous cases there is no marked increase of solubility near a transition temperature, because the (concealed) congruent melting point is too far distant.

Summary

The graph obtained on plotting the logarithms of the aqueous pressures of saturated solutions against reciprocal temperatures may show many types of slope, and extreme or even retroflex curvature. The slopes of such curves are interpreted by means of an equation suggested by Roozeboom, which is applied to experimental data which were lacking in his day.

PRINCETON, N. J.

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[16] Kracek, *J. Wash. Acad. Sci.*, **26**, 307 (1936).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE RICE INSTITUTE]

The Nephelometric End-point of Atomic Weight Titrations

BY ARTHUR F. SCOTT AND FRANK H. HURLEY, JR.

The well-known Harvard method for determining atomic weights by the analysis of pure halogen compounds is essentially a titration process in which the halide ion in the analytical sample is precipitated by silver ion, the end-point being found by nephelometric tests. In making these tests of the relative amounts of silver and halide ions in the analytical solution, two equal, small samples of the solution are withdrawn; the halide content of one is precipitated as silver halide by the addition of silver ion, the silver content of the other is precipitated also as silver halide by the addition of an excess of halide ion. The small amounts of silver halide precipitated in these test samples remain in suspension for some time and their turbidities or opalescences are assumed to be proportional to the concentration of halide and silver ion, respectively. In accordance with this basic assumption equivalence of silver and halide in the titration process is assumed to have been attained when the corresponding opalescences of "excess Ag" and "excess X" test samples are equal. Recent discussions[1] of this "equal-opalescence" end-point for chloride analyses have cast doubt on its validity, and have indicated the need of further experimental study. Some new experiments bearing on this problem have been carried out and will be described in this report.

The conflicting evidence with regard to the validity of the chloride "equal-opalescence end-point" can be resolved in part by distinguishing between two different types of end-points as they have been developed in practice; first, the end-point established in the case of solutions which

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[1] Johnson, *J. Phys. Chem.*, **35**, 540, 2237 (1931); **36**, 1942 (1932); **39**, 781 (1935); Johnson and Low, *ibid.*, **36**, 2390 (1932); Briscoe, Kikuchi and Peel, *Proc. Roy. Soc.* (London), **A133**, 440 (1931).

have come to equilibrium at room temperature (R^- end-point); and second, the end-point of solutions which have been kept at ice temperature (I^- end-point). The only difference between the conditions of these two end-points is, of course, the concentration of the dissolved silver halide at the time of the nephelometric tests.

The validity of the R^- end-point appears to be fully substantiated. This conclusion is based on experiments with artificial analytical solutions which are prepared by allowing carefully purified silver chloride to come into equilibrium with a solution containing such quantities of nitric acid and other substances as would be present in a real analytical solution. Nephelometric tests[2] of these artificial analytical solutions have always shown "equal opalescence" within the possible limits of error.

Although the I^- end-point has been and still is employed as much as the R^- end-point, tests of its validity comparable to those of the R^- end-point, were not made until a few years ago. The reason for this is clear from the following account of the development of the I^- end-point. Subsequent to the success of the R^- end-point in chloride analyses, the same procedure was applied to similar bromide analyses and it was found that the lower solubility of the silver bromide enhanced greatly the sensitivity of the nephelometric tests. To gain this same advantage for chloride analyses, the I^- end-point was adopted.[3] So far as the writers can ascertain no direct test of either the bromide or I^- end-point was made at the time these end-points were introduced. Their validity, apparently, was taken for granted because of the previous proof of the validity of the R^- end-point.

A direct test of the I^- end-point by analyzing artificial analytical solutions was made recently, for the first time, by Johnson.[4] His experiments, contrary to the results obtained for the R^- end-point, showed that the opalescences of the "excess Ag" and "excess Cl" suspensions are not equal, that there is an apparent excess of chloride in the solution saturated with pure silver chloride. Baxter and his co-workers subsequently reported[5] tests of the I^- end-point which failed to confirm Johnson's experiments. It should be noted, however, that the conditions of the two tests were not identical. Baxter and his collaborators, instead of preparing artificial analytical solutions, used real analytical solutions which had been brought to the equal-opalescence end-point at room temperature. Cooling these solutions to the temperature of an ice-bath (I^- end-point) had no effect on the opalescence ratio.

The foregoing résumé has been presented not only to indicate the uncertain status of the "equal-opalescence" end-point but also to bring out the fact that the uncertainty arises from the rather surprising lack of a systematic study of the problem. For example, although the difference between the R^- end-points and the I^- end-points would appear to be simply one of concentration of silver chloride, there has been no investigation of the effect of this variable on the opalescence ratio. It was with intention of partially filling this gap that the present experiments were made.

To avoid repetition of details in the description of these experiments it may be noted here that they were carried out with as much care as if they were part of atomic weight analyses. The reagents and materials used were purified according to procedures employed in atomic weight work and in all mechanical operations great pains were taken to avoid the introduction of impurities, particularly dust. All nephelometric measurements were made with a nephelometer of the Richards type. The values of the opalescence ratios (opalescence of the "excess Ag" suspension to that of the "excess Cl" suspension) tabulated throughout this paper are the means obtained from ten settings of the right-hand jacket by alternately raising and lowering it until its field matched that on the left, which was held fixed. Other comparison ratios are the means of five settings made in a similar manner. All nephelometric test suspensions were prepared by the "uniform" method[6] of mixing, using 20-ml. portions of the test solutions and 2-ml. portions of the precipitants, which contained 1.000 g. of silver or its equivalent of sodium chloride in a liter of solution. The nephelometric comparisons were made one hour after the suspensions were prepared. To get some idea of the reproducibility of the suspensions prepared by this "uniform" method of mixing under the conditions of the present experiment, we occasionally prepared within a few minutes of each other two or more pairs of suspensions from the same test solution. The mean value of the "average deviation" of nine such duplicate measurements was only 0.6%.

Our first experiment was a direct test of the I^- end-point. Three samples of pure, well-washed silver chloride were covered with 0.16 *M* nitric acid and allowed to become saturated at room temperature. The three saturated solutions were then treated in the following manner. (1) Samples of each solution were withdrawn at 31.5° and

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(2) Richards and Wells, THIS JOURNAL, **27**, 505 (1905); Scott and Johnson, *ibid.*, **52**, 2644 (1930); and *J. Phys. Chem.*, **33**, 1975 (1929); Johnson, *ibid.*, **35**, 2237 (1931).

(3) Richards and Willard, THIS JOURNAL, **32**, 4 (1910).

(4) Johnson, *J. Phys. Chem.*, **36**, 1942 (1932); Johnson and Low, *ibid.*, **36**, 2390 (1932).

(5) Baxter and Alter, THIS JOURNAL, **55**, 2789 (1933); Baxter and MacNevin, *ibid.*, **55**, 3187 (1933).

(6) Scott and Hurley, *ibid.*, **56**, 333 (1934).

filtered through a sintered glass filter directly into small bottles where they were stored. (2) The saturated solutions were then placed in a bath of crushed ice and allowed to stand with occasional shaking for a period of nineteen hours, after which samples were withdrawn and filtered as before. The temperature at the time of withdrawal was 0.5°. (3) The solutions were then frozen by means of an alcohol–carbon dioxide mixture, and allowed to melt. As soon as they were completely liquid, they were again placed in the ice-bath for one and one-half hours without agitation. Samples of these solutions were also withdrawn and filtered into bottles. The temperature was 0.7°. (4) The solutions were removed from the ice-bath and allowed to stand overnight at room temperature. Samples were then taken as before.

The bottles in which the samples were collected were rinsed with a small amount of the sample to be collected. All the samples were allowed to stand for two days at room temperature before nephelometric measurements were made. The samples of (2) and (3) were clear to the naked eye immediately after withdrawal, but when placed in a strong beam of non-actinic light gave a pronounced Tyndall cone, showing that a portion of the silver chloride precipitated from the solution by cooling remained suspended in the liquid. After the samples reached room temperature, no cone was observed, indicating that the suspended silver chloride had dissolved.

Measurement of the opalescence ratios (opalescence of the "excess Ag" suspension to that of the "excess Cl" suspension) gave the results summarized in Table I.

TABLE I

OPALESCENCE RATIOS OF ARTIFICIAL ANALYTICAL SOLUTIONS UNDER DIFFERENT CONDITIONS

Sample no.	Withdrawn from soln. saturated at	Soln. A	Soln. B	Soln. C
1	Room temp.	1.07	1.05	1.00
2	0.5°	1.52	1.24	1.40
3	.7°, after freezing		1.79	1.53
4	Same as (1)	1.05	1.03	1.00

As can be seen from the table the opalescence ratios of these artificial solutions in the neighborhood of 0° (I^- end-point) are much greater than unity and are in accord with the findings of Johnson.[4] Furthermore, since a ratio approximately equal to unity is found for the solutions at room temperature these measurements are also in agreement with previous tests of the R^- end-point. To determine whether the concentrations of silver and chloride in sample no. 4 differed from those in sample no. 1, the "excess Ag" as well as the "excess Cl" suspensions of samples 1 and 4 were intercompared. These intercomparison ratios were sensibly unity, indicating that the concentration of silver chloride in sample 1 was restored in sample 4.

There are two possible explanations of the variation of the opalesence ratio with the temperature of the analytical solution. (1) In the solutions at ice temperature there is a real excess of chloride ion due to the preferential adsorption of silver ion on the silver halide particles which are precipitated when solutions saturated at room temperature are cooled to ice temperature. (2) The concentrations of silver and chloride ions in the saturated solutions are equal at both temperatures but the opalescences of the "excess Cl" suspension and the "excess Ag" suspensions do not vary in the same manner with changing concentration. This would mean that the assumptions underlying the "equal-opalescence" end-point are not generally valid.

An experiment which affords a test of both of the foregoing explanations was carried out as follows. Standard solutions containing carefully measured, equivalent amounts of silver nitrate and sodium chloride were made up to cover a wide range of silver chloride concentrations in small steps. Three series of these standards, each containing different amounts of nitric acid, were prepared. In making nephelometric measurements of these standard solutions, the following procedure was adopted. For a set of measurements the necessary pair of test samples was withdrawn from two standard solutions, the silver chloride concentration of which differed by one step. After the opalescence ratio of each standard solution had been determined, the "excess Ag" suspensions of the adjacent standards were intercompared. Each set of measurements, starting with the withdrawal of the test portions, was made at least twice. In the following discussion only the mean of these duplicate measurements will be considered.

The results of these experiments are summarized in Tables II and III which are self-explanatory.

TABLE II

OPALESCENCE RATIOS OF STANDARD SOLUTIONS CONTAINING EQUIVALENT AMOUNTS OF SILVER AND CHLORIDE IONS

Concn. of Ag^+ and Cl^- in mg. Ag per liter	0.32 *M* HNO_3	0.16 *M* HNO_3	0.0064 *M* HNO_3
0.4	1.52		
.6	1.47	1.47	1.77
.8	1.45	1.25	1.20
1.0	1.18	1.23	1.20
1.2	1.08	1.11	1.08
1.4		1.10	1.05
1.6		1.08	1.08
1.8		1.05	1.05
2.0		0.99	1.03

TABLE III

INTERCOMPARISON RATIOS OF "EXCESS AG" SUSPENSIONS

Standards compared	Ratio of concn.	0.0064 *M* HNO_3	0.16 *M* HNO_3
0.8/0.6	1.33	1.38	1.34
1.0/0.8	1.25	1.43	1.44
1.2/1.0	1.20	1.39	1.25
1.4/1.2	1.17	1.21	1.34
1.6/1.4	1.14	1.18	1.24
1.8/1.6	1.13	1.08	1.17
2.0/1.8	1.11	1.16	1.09

We may note first that the opalescence ratio values obtained with these standard solutions (Table II) are in good agreement with those obtained with the saturated solutions. Thus, the most concentrated standard (0.16 *M* nitric acid) has practically the same concentration of silver chloride as a saturated solution at room temperature and its opalescence ratio is unity like those of samples 1 and 4 described in Table I.

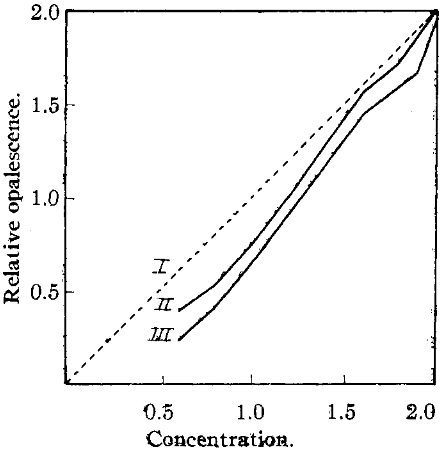

Fig. 1.—Showing variation of opalescence with concentration of silver chloride for (II) excess silver and (III) excess chloride suspensions. Line I shows the assumed variation.

Further, the 0.6-mg. standard solution has approximately the concentration of a saturated solution of silver chloride in 0.16 *M* nitric acid at 0°; its ratio 1.47 is of the same order of magnitude as the mean values of this ratio 1.39 and 1.66 found in the case of the corresponding saturated solutions 2 and 3 described in Table I. Since no solid silver chloride was present in the standard solutions which yielded the high ratio values, the high values found with the artificial analytical solutions cannot be attributed to adsorption of silver ion by the colloidal precipitate.

Having eliminated this first possibility of accounting for the high ratio values we may now turn with a greater degree of confidence to a consideration of the alternative explanation. The relationship between concentration and opalescence of the test suspensions, as found with the standard solutions, is depicted in Fig. 1. In constructing this graph the opalescence of the "excess Ag" suspension prepared with the 2.0-mg. standard was arbitrarily assigned a value of 2.0. Starting with this value, the relative opalescences of the other "excess Ag" suspensions were calculated by means of the intercomparison ratios given in Table III. The relative opalescences of the "excess Cl" suspensions were then calculated from the corresponding "excess Ag" opalescences by means of the ratios given in Table II. The relative opalescence values used in the figure are the averages of the values obtained for the standard solutions which were 0.16 and 0.0064 molar with respect to nitric acid.

This opalescence–concentration plot shows two things regarding the opalescences of test suspensions: (1) that the opalescence is not directly proportional to the concentration of the ion precipitated, and (2) that the relationship between opalescence and concentration is not the same for "excess Ag" and "excess Cl" suspensions. In other words, the assumptions on which the acceptance of the equal-opalescence end-point rests are not strictly true.

It should be noted, however, that the discrepancy between the actual conditions and those assumed in accepting the equal-opalescence end-point depends on the concentration of silver chloride. The discrepancy is greatest at low concentrations of silver chloride and becomes negligible as the concentration of silver chloride approaches that of a saturated solution at room temperature. It is therefore an unfortunate coincidence that the only tests of the equal-opalescence end-point which had been made until recently should have been carried out with solutions saturated with silver chloride at room temperature.

Although no attempt will be made at this time to develop a detailed explanation of the nature of the opalescence–concentration relationships, a few points will be outlined to show that the observed relationships can be accounted for on quite plausible grounds. We may note at the outset that the non-linearity of the opalescence–concentration relationship is in general agreement with the results of other investigators.[7]

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(7) Kober and Egerer, THIS JOURNAL, **37**, 2373 (1915).

The occurrence of the more complex relationship arises from the fact that the opalescence of a suspension depends not only on amount of material precipitated but on other factors such as the size of the precipitated particles. The difference between the opalescence-concentration relationships of the "excess Ag" and "excess Cl" suspensions becomes understandable when it is recalled that silver chloride is more soluble in solutions containing excess chloride than in those containing a similar excess of silver. For, as a result of this greater solubility of silver chloride in the "excess Cl" suspension less material would be precipitated than in the corresponding "excess Ag" suspension. At high concentrations of silver chloride the difference between the amounts of material dissolved in the two suspensions would be negligible relative to the total quantity of material precipitated. But with smaller concentrations of silver chloride this difference would become increasingly significant, and the "excess Cl" suspension, having less material in suspension, would have less opalescence than the corresponding "excess Ag" suspension.

The fact that the true opalescence ratio for solutions containing equivalent amounts of silver and chloride is not unity for all concentrations of silver chloride means that the acceptance of equal-opalescence as the end-point in the titration of chloride with silver is a potential source of error in atomic weight analyses. Since we have found the opalescence ratio at the true end-point to deviate from unity only in one direction, the error, if it occurs, would always result in the addition of more than the stoichiometrical amount of silver. The magnitude of the error would depend, of course, on the deviation of the true opalescence ratio from unity; it would be appreciable only in analyses at the I^- end-point.

This conclusion, it is important to note, is based on experiments with solutions which contained little or no colloidal silver chloride in suspension, and is directly applicable, therefore, only to analytical solutions which are practically free from colloidal precipitate. Since this condition is not necessarily fulfilled by real analytical solutions, we shall consider briefly the probable effect of colloidal precipitate on the nephelometric measurements.

The way in which colloidal precipitate suspended in analytical solutions at the I^- end-point would affect the nephelometric measurements is pictured easily. Since the nephelometric test samples taken from these solutions are brought to room temperature before the test suspensions are prepared, any colloidal material present would dissolve prior to the precipitation of the test suspensions. By increasing the effective concentration of silver chloride in the test samples, colloid would act to bring the true opalescence ratio nearer to unity and would accordingly reduce the magnitude of the end-point error.

No information as to the amount of colloidal precipitate in real analytical solutions is available and consequently no estimate of the magnitude of the end-point error can be made for any particular set of atomic weight analyses. In general, however, it would seem reasonable to suppose that real analytical solutions contain some colloidal material: they contain freshly formed precipitate which is mostly in the colloidal state and which, at ice temperature, would age slowly. The additions of small amounts of silver or chloride required to bring the solution to the end-point would also produce fresh colloidal material during the course of the nephelometric tests. Furthermore, the accepted practice of shaking the analytical solutions vigorously before the withdrawal of the test samples would act to ensure the continued suspension of precipitate in colloidal form. Some indirect evidence that the solutions of atomic weight analyses contain colloidal material is to be found in observations recorded in the published reports. For example, Baxter and Grover[8] abandoned the I^- end-point and returned to the R^- end-point because "we found that the accuracy of our experiments was not perceptibly increased by the (cooling) process." Likewise, the failure of Baxter and his co-workers[5] to detect a change in the opalescence ratio on cooling real analytical solutions can be accounted for most plausibly on the assumption that these solutions contained a large quantity of colloidal precipitate.

In view of the probability that real analytical solutions contain colloidal precipitate, we must conclude that the magnitude of the end-point error in atomic weight analyses is in general less than that indicated by Johnson's and our experiments with artificial analytical solutions. Indeed, the fact that there is no consistent difference between the results of analyses at the I^- and R^- end-point would suggest that solutions of many

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[8] Baxter and Grover, THIS JOURNAL, **37**, 1027 (1915).

atomic weight analyses have contained so much colloid that the error in question is negligibly small. The only analyses about which there need be serious concern at present are two[9] which have been used to establish the ratio between silver and oxygen.

Summary

Tests of the nephelometric end-point of atomic weight titrations using saturated solutions of silver chloride have shown that the end-point of equal opalescence, although valid at room temperature, is not correct when the solutions are cooled to 0°, for at this temperature the solutions show an apparent excess of chloride over silver. Experiments made in the absence of solid silver chloride show that the apparent excess of chloride cannot be attributed to adsorption by the precipitate, but must instead be due to the fact that the opalescences of the nephelometric suspensions are not strictly proportional to the concentrations of silver and chloride in the solutions. A possible explanation for this behavior on the basis of the increased solubility of silver chloride in solutions containing excess chloride is suggested, and the effect of colloidal silver chloride on the end-point is considered briefly.

HOUSTON, TEXAS RECEIVED MAY 11, 1937

(9) Richards and Willard, THIS JOURNAL, **32**, 48 (1910); Hönigschmid and Sachtleben, *Z. anorg. Chem.*, **178**, 1 (1929).

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Studies in the Phenanthrene Series. XV. Observations on Substitution in 9,10-Dihydrophenanthrene: Tetracyclic Compounds Derived from It[1]

BY ALFRED BURGER AND ERICH MOSETTIG

The convenient method of preparation of 9,10-dihydrophenanthrene (I) recently published from this Laboratory[2] has enabled us to prepare a large number of derivatives of this hydrocarbon, which have been tested for pharmacological action.[3] In continuation of this work, the feasibility of introducing other substituents suitable for further synthetical experiments has been investigated. We have pointed out that in the Friedel–Crafts reaction on 9,10-dihydrophenanthrene the acetyl or propionyl group enters position 2 exclusively, whereas in phenanthrene itself these groups enter chiefly position 3, while position 2 is attacked only to a minor extent.[4]

2-Acetyl-9,10-dihydrophenanthrene (II), which can be prepared readily in large quantities, furnishes a convenient starting material for the preparation of the 2-amino compound by the Beckmann rearrangement of its oxime, a procedure that has been applied very recently and independently by several investigators to the preparation of phenanthryl amines.[5]

9,10-Dihydro-2-dimethylaminophenanthrene is obtained with great ease by thermal decomposition of its methiodide. 2-Hydroxy-9,10-dihydrophenanthrene may be obtained from the amino compound by means of the diazo reaction.

In the Friedel–Crafts reaction with succinic anhydride as well as in the noteworthy method of Hinkel and co-workers for introducing the aldehyde group into aromatic hydrocarbons[6] the respective substitutents enter, as was to be expected, position 2 of 9,10-dihydrophenanthrene. Whereas β-[2-(9,10-dihydrophenanthroyl)]-propionic acid (III) can be obtained in excellent yields, the yield of 9,10-dihydrophenanthrene-2-aldehyde (VI) could not be raised above 30%. In both instances no isomeric acid, or aldehyde, respectively, could be detected in the reaction mixtures. The structure of the acid (III) could be proved by synthesizing it by another route, namely, from 2-ω-bromoacetyl-9,10-dihydrophen-

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(1) The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

(2) (a) Burger and Mosettig, THIS JOURNAL, **57**, 2731 (1935); (b) *ibid.*, **58**, 1857 (1936). See also Durland and Adkins, *ibid.*, **59**, 135 (1937).

(3) Nathan B. Eddy, Department of Pharmacology, University of Michigan, unpublished results.

(4) Mosettig and van de Kamp, THIS JOURNAL, **52**, 3704 (1930); Bachmann and Struve, *ibid.*, **58**, 1659 (1936).

(5) Adelson and Bogert, *ibid.*, **58**, 653 (1936); Bachmann and Boatner, *ibid.*, **58**, 857, 2097 (1936); Mosettig and Krueger, *ibid.*, **58**, 1311 (1936).

(6) (a) Hinkel, Ayling and Morgan, *J. Chem. Soc.*, 2793 (1932); (b) Hinkel, Ayling and Beynon, *ibid.*, 184, 339 (1936).