A STUDY OF THE POTASSIUM DITHIO-OXALATE COLORIMETRIC METHOD FOR THE DETERMINATION OF NICKEL

BY JOHN H. YOE AND FLOYD H. WIRSING

Over twenty years ago Jones and Tasker[1] reported a method for making potassium dithio-oxalate, $K_2C_2O_2S_2$. They found that this substance gives intense colors in water solution with certain metallic salts. Among these they discovered that nickel salts give a deep magenta color in dilute solutions. If equal weights of potassium dithio-oxalate and a soluble nickel salt are mixed in concentrated solutions there separate out small black needle-shaped crystals. These crystals color water more intensely than does potassium permanganate.

More recently, Fairhall[2] has employed potassium dithio-oxalate to determine nickel colorimetrically. The reagent is extremely sensitive and thus permits the determination of very small amounts of nickel. Fairhall made determinations on biological materials which contained small known quantities of nickel and obtained results accurate to a fraction of a milligram. His results indicated that potassium dithio-oxalate possessed advantages over other colorimetric reagents for nickel, such as dimethylglyoxime and α-benzyl-dioxime. These advantages are greater sensitiveness and better formation of color.

The purpose of this investigation was to study the reaction between potassium dithio-oxalate and nickel with reference to its use in the colorimetric determination of nickel. The sensitivity of the reaction, application of Beer's law, effect of various ions and different experimental conditions have been studied.

Apparatus and Reagents.—The apparatus and general technique have been described in a paper by Yoe and Hill.[3] A Bausch and Lomb Duboscq colorimeter was used in place of the Kennicott–Campbell–Hurley instrument employed by Yoe and Hill. The Nessler tubes measured 210 mm. to the 50 ml. mark. All weights and volumetric instruments were calibrated.

The potassium dithio-oxalate was obtained from the Eastman Kodak Co. Freshly boiled distilled water was used to make up the reagent solution. A stock solution of nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$, was prepared and its concentration determined gravimetrically by the dimethylglyoxime method. The average of three closely agreeing results gave 0.9998 g. of

[1] Jones and Tasker, *J. Chem. Soc.*, **95**, 1904–9 (1909).

[2] Fairhall, *J. Ind. Hygiene*, **8**, 528–34 (1926).

[3] Yoe and Hill, THIS JOURNAL, **49**, 2395–2408 (1927).

nickel per liter at 20°.   Ten ml. of this solution was diluted to a liter and thoroughly mixed.   One ml. of the diluted solution contained 0.01 mg. of nickel and was taken as the standard solution.

Experimental

In the first part of our work a series of eight "unknowns" containing nickel was analyzed.   These were checked several times, totaling about 1000 readings for practice in colorimetric measurements with the potassium dithio-oxalate reagent.

The following order of addition of reagents was adopted and observed throughout the investigation.   Ten ml. of each of the nickel solutions were pipetted into the colorimeter cups and the required volumes of reagent added according to the concentration of the nickel.   The same pipets were always used and they were rinsed out with the solution before the aliquot was taken.   One of the cups was marked and it always contained the standard nickel solution, which occupied the left side of the colorimeter. After adding the reagent, the solutions were stirred with separate glass rods.   These were bent into a triangle at the end to give more efficient stirring.   The solutions were compared immediately.

A measurement required from ten to fifteen minutes.   The temperature of the dark room was approximately 25°.   The number of readings on the colorimeter for each solution was at least six.   These were alternated, one being made as the height of the adjustable column of liquid was increased and the next as the height of the column was decreased.   The total number of readings depended on how well they checked, more being taken if they did not agree closely.   Usually eight or ten readings were made and the average taken.

To facilitate calculations the "unknown" solutions were set at some easily divisible number as 10, 20 or 30, and the standard adjusted to match this.   The calculation was simply

$$\frac{\text{Reading of standard}}{\text{Setting of unknown}} \times \text{concn. of standard} = \text{mg. of nickel per ml. of unknown.}$$

Beer's Law.—Beer's law may be stated as follows.   When equal heights or thicknesses of two solutions give the same intensity of color, the concentrations are equal.   When equal color intensity is obtained from different heights of two solutions, the concentrations are inversely proportional to the heights, in accordance with Beer's law.   This relationship forms the basis for colorimetry.   In order for it to hold, the color formation in the two solutions must be perfectly formed, or imperfectly formed to the same extent in both solutions.   It is sometimes the case in colorimetric analysis that the color formation is incomplete or unstable.   This must be overcome by a calibration or correction curve which can be prepared experimentally from solutions of known concentrations.

The stock solution was used to make nickel solutions of various concentrations. The nickel solution to be diluted and the distilled water used were at 20 ± 1°. The concentrations varied from 0.1 to 0.001 mg. of nickel per ml. Ten ml. of each solution was compared with ten ml. of standard nickel solution as explained above. The amount of potassium dithio-oxalate added to each wa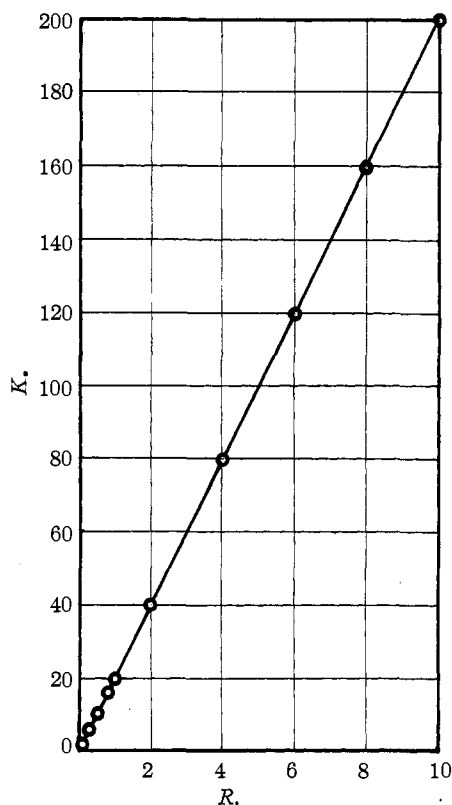s sufficient for complete color reaction, because each set of measurements was duplicated with a larger amount of reagent.

According to Beer's law a straight line is obtained by plotting the readings of the standards when the unknown solutions are set at 20.0, against the ratios of the height of standard over the height of unknown. Our results are shown graphically in Fig. 1. It is obvious that Beer's law is valid over the range in concentration studied and hence a correction curve is not required.

Sensitivity.—It is well known that in making color comparisons good results are not obtained with too deeply colored solutions. In practice, dilute solutions are either specified or implied. Horn[4] pointed out that the sensitiveness of solutions is a variable and that the ease of determination varies with the concentration. In general, it is believed that there is some one concentration at which a change in the intensity of the color can be more readily detected by the eye than at other concentrations. This concentration is in the range of dilute solutions. The *sensitivity* may be defined as *the reciprocal of the weight in milligrams of the constituent being determined that produces a change in color which can just be differentiated with certainty.*

Comparisons were made in a regular Nessler tube rack having a piece of black cardboard pasted on each side to shield the tubes from light. The solutions were made uniform by stirring. The colored solutions were measured from labeled pipets having 15, 10, 5, 3, 2 and 1 ml. capacity,

Fig. 1.

4 Horn, *Am. Chem. J.*, **35**, 253–9 (1906).

respectively. For smaller quantities a 2-ml. pipet graduated to 0.1 ml. was used. The comparisons were made in daylight reflected from a white porcelain surface placed below the Nessler tubes and at a 45° angle. The comparisons were made at any hour of the day that was convenient and in cloudy as well as clear weather.

The standard colored solution was made from 10 ml. of the nickel standard and 1.6 ml. of a 0.1% potassium dithio-oxalate solution. It was usually made up in 100 ml. amounts. Portions of the standard colored solution were pipetted into Nessler tubes, each differing by a constant amount. These were then made up to 50 ml. with distilled water from a buret, and stirred thoroughly with a glass rod. The Nessler tubes were corked to prevent contamination. Different symbols and numbers were used so as not to indicate the arrangement to the observer. To avoid fading, comparisons were always made within two hours after the solution was prepared. Each series of tubes was compared and arranged in order of depth of color by five (occasionally four) observers. At another time these same concentrations, but freshly prepared solutions were arranged. This was repeated if the results were not in agreement with the first ones. In all cases the solutions were made and arranged out of order by one of us (F. H. W.) who was not making the comparisons.

The procedure followed was to pipet portions of the standard colored solution into the Nessler tubes, starting with zero ml. and increasing each by one ml. up to 12. These were always arranged in correct order. Then with a fresh solution, tubes were made each differing by the increment of half a ml. of colored solution. These were arranged in perfect order until the 10 ml. concentration was reached, when one observer could not tell the difference between the two tubes containing 10.0 and 10.5 ml., respectively. At this concentration, 0.5 ml. was the increment of colored solution which produced a change in color that could just be differentiated with certainty. Less labor was involved by working from one concentration, as 3 ml. of

TABLE I

MEASUREMENTS AND CALCULATED RESULTS

1	2	3	4	5	6	7	8	9
V	B	Δ	S	B'	Δ/B'	B/B'	$\sqrt{V}$	$\sqrt{S}$
34,930	0.0840	0.00420	238	0.08820	0.0476	0.953	187	15.42
43,675	.0672	.00336	297	.07056	.0476	.953	209	17.23
58,210	.0504	.00252	396	.05292	.0476	.952	241	19.90
87,320	.0336	.00168	595	.03528	.0476	.952	295	24.39
116,400	.0252	.000840	1190	.02604	.0322	.967	341	34.50
298,200	.00984	.000492	2032	.01033	.0476	.952	546	45.06
372,700	.00787	.000394	2538	.008266	.0476	.953	610	50.37
497,800	.00590	.000295	3390	.006198	.0476	.953	705	58.22
475,400	.00394	.000197	5075	.004133	.0476	.954	863	71.23
1,490,000	.00197	.000197	5075	.002165	.0909	.929	1220	71.23
9,314,000	.00033	Matched solution to which no nickel had been added.						

colored solution and 47 ml. of water. Other solutions were made up containing 2.8, 2.9, 3.0, 3.1 and 3.2 ml., respectively. In arranging these, no tube was out of order by more than one place. At this concentration, the amount which produces a perceptible difference is 0.1 ml. Solutions differing by less than a tenth of a ml. were not attempted. In weaker concentrations, say two ml. of colored solution, tubes having 1.8, 1.9, 2.0, 2.1 and 2.2 ml. were always arrange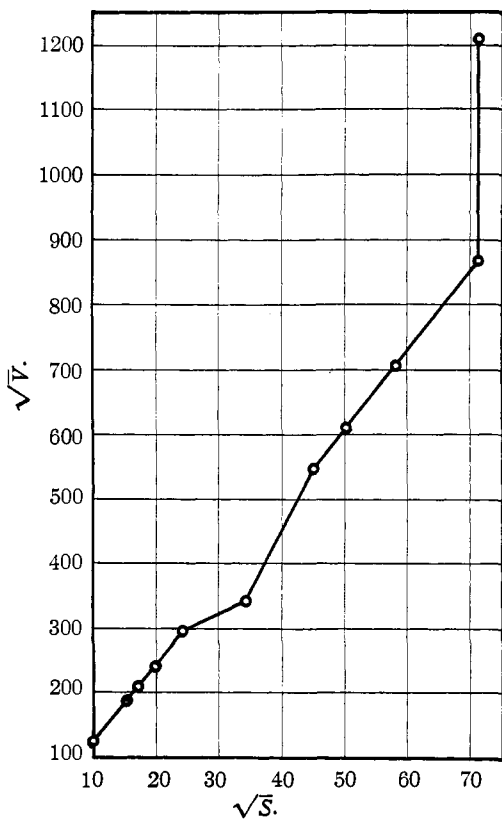d in correct order. Hence a standard nickel solution containing 0.001 mg. per ml. was used for smaller concentrations. This procedure was repeated for a number of concentrations. The measurements and their calculated results are recorded in Table I.

Column 1 gives the volume in liters containing one gram atom of nickel. In the second column B is the total milligrams of nickel in 50 ml. of solution. In column 3 Δ is the mg. of nickel producing a perceptible difference in the color intensity of 50 ml. of solution. $S = 1/\Delta =$ Sensitivity. $B' = B + \Delta$.

Figure 2 shows how the sensitivity varies with the concentration. In plotting the curve the square roots of the volume and of the sensitivity are used to make the graph less extensive. The sensitivity curve obtained for nickel is very similar to those obtained for other metals. Horn and Blake[5] made sensitivity curves for Cu^{++} and CrO_4^{-} ions. Yoe and Hill[6] obtained sensitivity curves for aluminum by both the Aluminon and Alizarin Red S methods. The sensitivity of the Cu^{++} and CrO_4^{-} ions increases greatly at a definite concentration, as shown in the curves of Horn and Blake. This is not true in the case of aluminum or nickel. Except for a slight break (maximum sensitivity range) in the curve for nickel and at

Fig. 2.

[5] Horn and Blake, *Am. Chem. J.*, **36**, 195–208 (1906).

[6] Yoe and Hill, THIS JOURNAL, **49**, 2395–2408 (1927); **50**, 748–756 (1928).

very dilute solutions, the sensitivity is a straight line function of the concentration. The setting of the standard nickel solution should be made at a point on the colorimeter scale which is within the range of maximum sensitivity.

The data in columns 6 and 7 show that over a wide range in concentration the ratios Δ/B' and B/B' are approximately constant. These ratios are also constant in the work of Horn and Blake and of Yoe and Hill. Δ/B' is the ratio between the amount of nickel which just suffices to produce a distinguishable difference in color, and the total amount of nickel present in 50 ml. of solution. This ratio is a constant except in too dilute solutions and where there is a break in the sensitivity curve. Horn and Blake[5] have shown that this value multiplied by 100 gives directly the percentage error inherent in the comparison of colors. Other sensitivity data show that the colored solutions may be too dilute, as well as too concentrated, to give the best results.

That the ratio Δ/B' is a constant follows from Weber's[7] psycho-physical law which states that a sensation is proportional to the natural logarithm of the stimulus, or that the increase of a stimulus necessary to cause an increase in sensation is a constant fraction of the whole stimulus. It is reasonable to assume that the stimulus is proportional to the amount of colored solute (or nickel) present. By definition, the sensitivity of the eye is a small increase in the sensation. From a mathematical consideration, Weber's law becomes

	Sensation	$= k \ln \text{stimulus}$	
Differentiating	d Sensation	$= k \, d \ln \text{stimulus}$	(1)
From Weber's law	Sensitivity of eye	$= d \text{ sensation} = \text{constant} = k_1$	(2)
Assumption	Stimulus	$= k' \text{ concentration}$	(3)
Substituting (2) and (3) in (1)	Sensitivity of eye $= k_1 = k \, d \ln k' \text{ concentration}$		
	$= K \, d \ln \text{concentration}$		
Since d concentration $= \Delta$	$= \dfrac{K\Delta}{\text{concentration}}$		(4)

Equation 4 is the statement of Fig. 2, namely, that the sensitivity, that is, $1/\Delta$, varies inversely as the concentration. Hence it follows that the ratio Δ/B' is a constant fraction of the total weight of nickel present.

B/B' is also constant and is the ratio between the total amounts of nickel in two 50-ml. tubes containing colored solutions that can just be distinguished with certainty. Horn and Blake[8] obtained for this ratio the average values of 0.92 and 0.95 for Cu^{++} ions and $[Cu(NH_3)_4]^{++}$ ions, respectively. They suggest the possibility that B/B' is a constant, independent of the color examined. This seems to be approximately true as indicated by all the known sensitivity work compiled in Table II.

[7] Hackh, "A Chemical Dictionary," P. Blakiston's Son and Co., Philadelphia, 1929.

[8] Horn and Blake, *Am. Chem. J.*, **36**, 516–22 (1906).

TABLE II

Ion	Method	Color	B/B', av. values	Observer
Al^{+++}	Aluminon	Red	0.92	Yoe and Hill
Al^{+++}	Alizarin	Red	.89	Yoe and Hill
CrO$_4$$^-$	CrO$_4$$^-$	Yellow	.96	Horn
Cu^{++}	Cu^{++}	Blue	.92	Horn and Blake
Cu^{++}	[Cu(NH$_3$)$_4$]$^{++}$	Dark blue	.95	Horn and Blake
Ni^{++}	K$_2$NiC$_4$O$_4$S$_4$	Magenta	.95	Yoe and Wirsing

In calculating B/B', values were omitted at each end of a series of measurements where the percentage error inherent in the comparison was large. This constant tends to become unity and its average value is usually above 0.90. In a series of measurements with solutions of any colored ion or molecule, the ratio B/B' approaches unity at the highest sensitivity. It is noted in the case of aluminum, using two different methods, but both giving approximately the same color, that the one with the higher average value of B/B' is the more sensitive.

The potassium dithio-oxalate–nickel reaction is very sensitive. Jones and Tasker[1] detected nickel at a dilution of one part in 40 million parts of solution, when the solution filled a beaker, and one part in 8 millions using a test-tube. Our experiments show that 0.008 mg. of nickel can be detected in a liter of solution, i. e., one part of nickel in 125 million parts of solution, when the observation is made in a 50-ml. (210-mm.) Nessler tube.

Optimum Experimental Conditions

In order to find the optimum experimental conditions, the effect of both the volume and the concentration of the reagent was determined. Ten ml. of standard nickel solution was compared with ten ml. of a nickel solution containing 0.008 mg. per ml. The reagent for the latter solution was added in small amounts and a comparison made after each addition until the intensity remained constant. The amount of reagent just sufficient for complete color formation was 1.2 ml. of a 0.05% K$_2$C$_2$O$_2$S$_2$ solution. This was repeated using a 0.1% reagent solution and 0.6 ml. was required. The weight of K$_2$C$_2$O$_2$S$_2$ was the same in both cases, but the volumes were different. Because of this unequal dilution of the nickel solution by the reagent, sufficient distilled water was added to the smaller volume to make the total volume of each the same.

A large excess of reagent causes a different shade or tint of color to develop, which is lighter than the red color of the potassium nickelo-dithio-oxalate. This fading appears more quickly for a large excess of reagent than for a small excess. Table III shows how quickly the fading appears when an excess of 0.1% reagent is used with 10 ml. of standard nickel solution.

TABLE III

Excess reagent, ml.	1.5	1.0	0.5	0.0
Time before fading, min.	15	30	75	300

With no excess reagent, fading is not very marked until the end of two days. However, with this concentration fading was never noticed under five hours and satisfactory readings have been made after twelve hours. The order of addition of reagents and nickel appears to make no difference, although it was always the same in this work.

Jones and Tasker represent the reaction of potassium dithio-oxalate with nickel salts by the equation: $2 K_2C_2O_2S_2 + NiX_2 = K_2(C_2O_2S_2)_2Ni + 2 KX$. The colored compound is potassium nickelo-dithio-oxalate, as shown by several analyses.

	Per cent. by analysis	Per cent. for $K_2NiC_4O_4S_4$
C	12.78	12.74
S	34.4	34.0
Ni	16.2	15.8

The theoretical amount of reagent required for a definite amount of nickel may be calculated from the above equation, and is 0.0675 mg. of $K_2C_2O_2S_2$ for 0.01 mg. of nickel. The amount of $K_2C_2O_2S_2$ experimentally required for 0.01 mg. of nickel was 0.080 mg. A solution of known nickel content was compared with the nickel standard. The reagent solution was added in small increments, a comparison being made after each addition. When the average reading on the colorimeter indicated the correct amount of nickel for the known solution, an excess of reagent never increased the intensity of the color. This procedure was repeated on a series of solutions of known nickel content.

The heavy line in Fig. 3 shows the amount of potassium dithio-oxalate required for various amounts of nickel as determined experimentally. The theoretical amount of reagent is shown by the
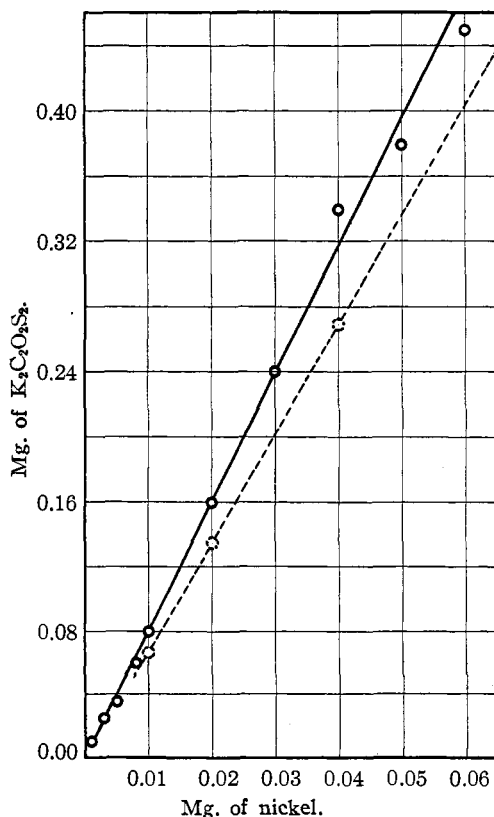

Fig. 3.

broken line.   It is evident that all of the reagent is not reacting with the nickel.   This is due to a slight decomposition of the reagent.

The instability of the potassium dithio-oxalate was the most trouble-some factor in this investigation.   The salt was light straw colored when obtained but gradually changed to brown.   Dilute solutions are colorless; concentrated ones are yellow.   Jones and Tasker reported that evaporation of the reagent solution on the water-bath gives a deposit of large colorless prisms.   The salt is white when recrystallized from alcohol, but on recrystallizing from water it becomes less stable.   On keep-ing, it turns brown.   The brown coloration does not seem to be due to the presence of sulfide or free sulfur.   Under the micro-scope particles of different color are visible, but these are very soluble in water.

After a reagent solution has stood for some time, there forms a yellow turbidity which gradu-ally settles out as a yellow pre-cipitate.   In the first part of our work measurements indicated that this did not appear so soon if the oxygen dissolved in the distilled water was boiled out before making the reagent up to volume.   It so happened that measurements with ordinary distilled water were carried out in the direct sunlight, while those with "oxygen-free" dis-tilled water were not.   Later m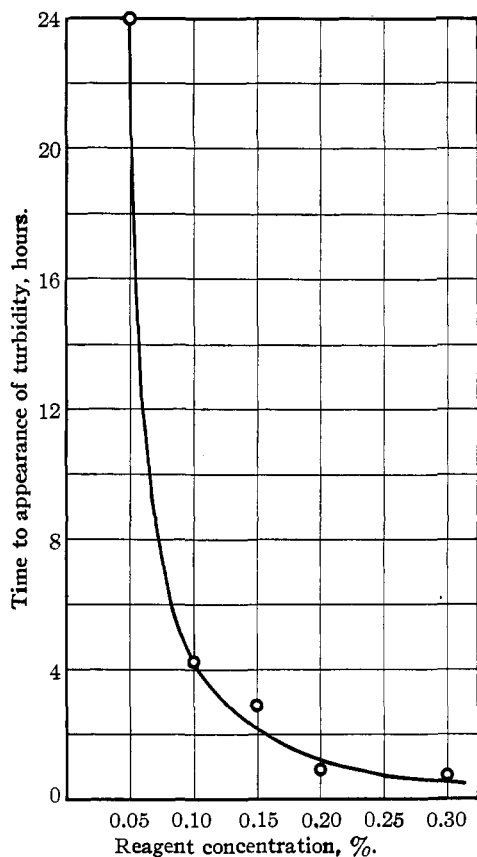easurements showed that sun-light produces cloudiness more readily than the oxygen in the water.   For example, a 0.3% reagent solu-tion made up with "oxygen-free" water showed no noticeable cloudiness in fifty minutes.   The same strength reagent made with ordinary distilled water and allowed to stand under the same conditions became noticeably turbid in forty minutes.   However, a portion of this same solution kept in the dark room was not cloudy in three days.

The curve in Fig. 4 shows the rate of appearance of turbidity in po-

Fig. 4.

Y-axis: Time to appearance of turbidity, hours.
X-axis: Reagent concentration, %.

tassium dithio-oxalate solutions at concentrations ranging from 0.05 to 0.30%. It is obvious that a 0.05% reagent solution is preferable to one more concentrated.

The stability of potassium dithio-oxalate in solution is affected by the hydrogen-ion concentration. An excess of hydrogen ions decomposes the reagent, while an excess of hydroxyl ions prevents it from becoming cloudy. For example, a 0.1% reagent solution in 0.002 N potassium hydroxide developed no turbidity upon long standing. In lower concentrations of alkali, turbidity appears more slowly than in neutral solution. Higher alkali concentrations cause the reagent solution gradually to turn yellow on standing for several weeks. Portions of a 0.1% reagent solution made acid with varying amounts of 0.1 N sulfuric acid all gave precipitates, the amount increasing with increase in acidity.   ·

Potassium nickelo-dithio-oxalate is relatively stable. Upon standing in solution for several weeks it loses its red color, but no cloudiness or precipitation appears. Its structural formula may be written as

$$\begin{array}{cc} O{=}C{-}S{-}K & O{=}C{-}S{-}K \\ | & | \\ O{=}C{-}S{-}Ni{-}S{-}C{=}O \end{array}$$
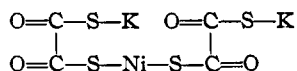
The effect of acidity or alkalinity on the colored potassium nickelo-dithio-oxalate solutions was observed by mixing 10-ml. portions of standard nickel solution with the required quantity of reagent and then adding varying amounts of acid or alkali. Alkali causes a fading of the colored solution. Even as small an amount as 0.2 ml. of 0.0174 N potassium hydroxide was sufficient to give incorrect colorimeter readings with 10 ml. of the standard nickel solution. Varying amounts of acid up to 0.8 ml. of 0.0194 N sulfuric acid in 10 ml. of standard nickel solution did not seriously affect the colorimeter readings but larger amounts gave a lighter shade of color than the characteristic pink. Hence, the final acidity of the colored nickel solution should not be over 0.002 N in sulfuric acid.

Effect of Various Ions.—Many metallic ions react with potassium dithio-oxalate to form colored compounds. Jones and Tasker observed color reactions with the following: Sb, Bi^{+++}, Cd^{++}, Co, Cu^{++}, Fe^{++}, Fe^{+++}, Mn, Hg^+, Hg^{++}, Ag^+, Sn^{++}, Sn^{++++}, Pd, Pt^{++}, Zn^{++}, Ce^{++++}, Au, Tl, Ti^{+++} and V. It is evident that any of the above ions may interfere with the nickel determination. Ions that give no color reaction are Al^{+++}, Ca^{++}, Ba^{++}, Sr^{++} and Mg^{++}. Iron and cobalt ions are the ones most likely to interfere with the nickel determination. Their concentration must be under one-hundredth that of the nickel; otherwise, an appreciable error results.

Summary

A study of the reaction between potassium dithio-oxalate and nickel has been made with reference to its use in colorimetry. The reaction obeys

Beer's law over a range in concentration suitable for colorimetric analysis. The sensitivity, optimum experimental conditions and the effect of various ions have been determined. Best results were obtained with a 0.05% reagent solution and a nickel concentration of ten mg. per liter. The reagent will detect one part of nickel in 125 million parts of solution, when the observation is made in a 50-ml. (210-mm.) Nessler tube. The color develops satisfactorily in sulfuric acid solution up to approximately 0.002 normal. Traces of alkali cause fading. Many metallic ions give color reactions with the reagent and hence will interfere with the nickel determination unless they are removed. Iron and cobalt are the ions most likely to interfere and must be removed unless the nickel concentration is at least a hundred times greater than that of these ions.

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THE HOMOGENEOUS COMBINATION OF ETHYLENE AND HYDROGEN. A SECOND-ORDER ASSOCIATION REACTION

BY ROBERT N. PEASE

It has recently been shown that the polymerization of ethylene at pressures above one atmosphere is a second-order homogeneous gas reaction.[1] The primary action is thus of the association type. In view of the fact that many homogeneous dissociation reactions are known to be first order, it was inevitable that second-order homogeneous association reactions should occur, unless the classical principle of mobile equilibrium is incorrect as ordinarily applied. Nevertheless, a theoretical difficulty has arisen in this connection which makes it especially desirable to investigate other cases. The hydrogenation of ethylene is a particularly suitable example since the reaction is reversible,[2] and the reverse action (dissociation of ethane) has been rather definitely shown to be first order.[3]

The theoretical difficulty mentioned above has to do with the accommodation of energy in a single product molecule newly formed by the collision of two reactant molecules. A rather crude analogy on a large scale is the cohesion of two "sticky" masses—say, two balls of tar—which have been directed at each other. In the latter case, any kinetic energy which is lost, and the cohesion energy are converted into internal energy of the resulting mass. Similarly in the case of two associating molecules, the

[1] Pease, THIS JOURNAL, **53**, 613 (1931). At lower pressures there is evidence of deviation. See Pease, *ibid.*, **52**, 1158 (1930). The polymerization of acetylene may also be second order. See Pease, *ibid.*, **51**, 3470 (1929).

[2] Pease and Durgan, *ibid.*, **50**, 2715 (1928).

[3] Marek and McCluer, *Ind. Eng. Chem.*, **23**, 878 (1931); Frey and Smith, *ibid.*, **20**, 948 (1928).