With a view to removing this uncertainty we have developed a method of investigating the diffusion of sodium vapor at temperatures considerably lower than that used by Hartel, Meer, and Polanyi. The complete investigation will take some time, and would include a study of the temperature coefficient of the diffusion constant and of the effect of adding various halides to the carrier gas. At present we wish to report our value for the diffusion coefficient of sodium in pure nitrogen at 253.5°C.

In the present method the diffusion takes place through a nickel capillary approximately 10 cm long and 3 mm i.d. A constant partial pressure of approximately 10^{-3} mm of sodium vapor was maintained at the lower end of the capillary from a pool of molten sodium in a 3-cm i.d. tube. The bottom of the larger tube was kept at a constant temperature somewhat lower than that of the capillary; a small intermediate furnace was used to eliminate cold spots. The sodium diffusing out of the capillary was continuously swept away by the circulating nitrogen and carried into an optical cell in which the absorption of sodium D resonance radiation was measured by a double photocell arrangement. The gradual darkening of the cell windows through the action of sodium vapor was allowed for by reversing the direction of nitrogen flow to take the "100 percent transmission" reading. The light absorption readings were correlated with sodium concentrations in calibration experiments in which the carrier gas was saturated with sodium vapor by passing over molten sodium at a series of known temperatures. The rate of diffusion of sodium out of the capillary was then calculated from the steady-state concentration of sodium in the carrier gas sweeping across the top of the capillary, and the flow rate of this gas. A correction term, amounting to 0.8 percent, was applied to take account of the diffusion in the 3-cm tube.

A total of six experiments were performed at 253.5 ± 0.1°C, using a nitrogen pressure of 4.3 mm. It is generally accepted that at such low pressures the diffusion coefficient is inversely proportional to the total pressure, and it is customary to express the results in terms of values calculated for a total pressure of one atmosphere. Our value, expressed in this way, was 0.68 ± 0.03 cm^2 sec^{-1} at 253.5°C and one atmosphere. Hartel, Meer, and Polanyi[3] quote a mean value of 0.91 cm^2 sec^{-1} at 382°C for their two experiments with pure nitrogen.

The new value of the diffusion coefficient is in good agreement with the one calculated from the data of Hartel, Meer, and Polanyi on the assumption of the $\frac{3}{2}$ power law, viz., 0.66 cm^2 sec^{-1} at 253.5°C. It would therefore appear that there was no serious error in using the earlier number for diffusion flame experiments at temperatures of this order. The problem still remains, however, of determining the exact law of temperature dependence and the influence of halide.

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Intramolecular Isotope Effects in the Decarboxylation of Malonic Acid*

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MALONIC acid, singly carboxyl-labeled with C^{14} by a modification of the method of Gal and Shulgin,[1] was decarboxylated at 138.0°C under 1 atmos of helium preheated to the same temperature. Acetic acid was removed from the gas stream by a dry ice trap, carbon dioxide by a liquid nitrogen trap. Acetic acid was burned to carbon dioxide over copper oxide. Samples of carbon dioxide were analyzed for C^{13} content determined with an ionization chamber-vibrating reed electrometer combination. Corrections and precautions described by Bigeleisen and Friedman,[2] and Lindsay, Bourns, and Thode[3] were applied.

In Table I are collected typical results, expressed as the ratio of rate of rupture of C^{12}—C^{12} bonds to that of C^{12}—C^x bonds,

TABLE I. Experimental values of k_4/k_3.

| | C^{13} effect | | C^{14} effect | |
	CO$_2$ basis	Acetic acid basis	CO$_2$ basis	Acetic acid basis
I	1.026	1.026	1.105	1.105
II	1.027	...	1.101	1.087

where x is 13 or 14; this ratio is k_4/k_3 in the notation of Bigeleisen and Friedman.

The C^{13} results are in agreement with those of previous investigations;[2,3] the C^{14} results are in essential agreement with the work of Yankwich and Calvin[4] but not with that of Roe and Hellmann.[5] The C^{14} results disagree with the predictions of Bigeleisen[6] and are not in much better correspondence with those of Pitzer.[7]

Preliminary experiments on bromomalonic acid indicate C^{13} and C^{14} isotope effects only slightly larger than those found for the unsubstituted acid.

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Near Infrared Absorption by Solutions of Inorganic Substances

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THE application of infrared absorption to the study of inorganic compounds has been of a rather limited nature.[1-3] Moreover, the infrared photometry of nearly "colorless" solutions is a well-nigh unexplored field. In the present communication an account of a preliminary study of some copper and nickel compounds, in the presence of some complex forming substances, is given.

The apparatus schematically depicted in Fig. 1 may be called a near infrared colorimeter. The light from a prefocus-type lamp,
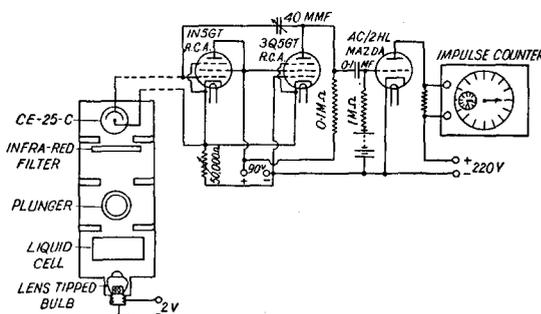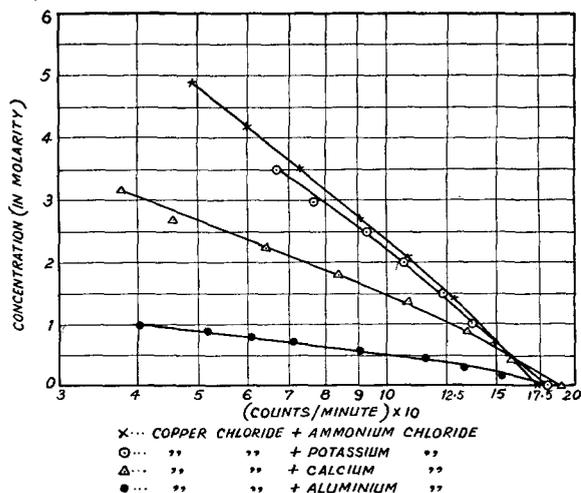

FIG. 1. Experimental arrangement.

FIG. 2. Change of absorption of cupric chloride 0.01M solution upon the addition of concentrations of various chlorides.

passing successively through a glass-cell containing the solution under examination, and a "Kodak" infrared filter, falls on a photo-emission cell (cesium-oxide cathode). A plunger bolt, which can be screwed up and down, regulates the amount of incident light. The photoemission cell is connected across the grid-input of a feed-back, relaxation oscillator. The intensity of the transmitted light is measured by the number of counts recorded by a suitable numerical counter in a certain interval of time, minus the background count during that interval. The background count can be made conveniently low, if care is taken to make the insulation of the input grid circuit sufficiently high. On account of the inherent characteristics of the cesium-oxide type photocell, the infrared region studied lies between 8000–11,000A units ($0.8–1.1\mu$).

The results obtained may be briefly stated as follows: Both the aqueous and the ammoniacal copper sulfate solutions appear to obey Beer's law. Absorption decreases by the addition of ammonia, which means that the complex cupri-ammonium ions are comparatively less opaque to the infrared region employed. Absorption curves for copper chloride, copper nitrate solutions show no difference from that of copper sulfate of the same concentration, within the region of dilution employed (0.01M).
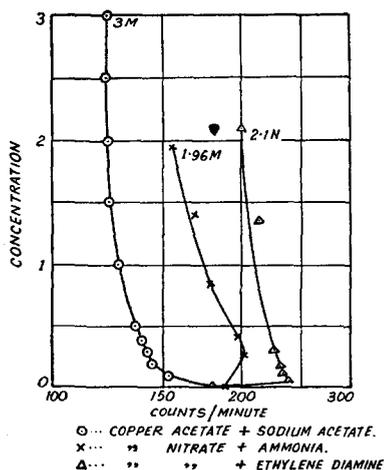
Both the aqueous and ammoniacal solution of nickel sulfate likewise obey Beer's law, but the nickel ammonium ion, on the contrary, shows a comparatively stronger absorption. No difference in absorption was observed between solutions of copper sulfate and copper ammonium sulfate, between those of nickel sulfate and nickel ammonium sulfate, or between ferrous sulfate and ferrous ammonium sulfate solutions.

Figure 2, shows the influence of ammonium chloride, potassium chloride, calcium chloride, and aluminium chloride upon the absorption by copper chloride solution (0.01M). As far as they have been studied the curves relating the concentration of the foreign chlorides with $\log I_0/I_t$ are all more or less straight. This seems to suggest the gradually increased formation of complex $[CuCl_4]''$ anion with the increased concentration of the chloride added. The complex tetra-chloro-cupric ion appears also to follow Beer's law.

Addition of increasing quantities of ammonium nitrate to a solution of copper nitrate shows no such change in absorption except a slight increase at very high concentrations of ammonium nitrate. Mercuric chloride added to a solution of copper chloride (0.01M) also shows no change in the absorption of the latter, obviously due to the non-ionic character of mercuric chloride. The absorption of nickel chloride solution, on the other hand, is not affected by the addition of ammonium chloride, potassium chloride, or aluminium chloride.

Figure 3 shows the influence of the addition of sodium acetate on the absorption of copper acetate and of ammonia and methylenediamine on that of copper nitrate. The curves give definite indication of complex formation. The breaks in the absorption curves for copper ammonia and copper ethylenediamine solutions seem to suggest stepwise formation of complexes in two stages which differ in their absorption power. The nickel chloride with ethylenediamine in aqueous solution, however, gives a continuous curve with continually increasing absorption with increasing ethylenediamine concentration, till a maximum is reached when it remains practically constant. Similar behavior was also observed with nickel chloride and pyridine solutions. The nickel ethylenediamine and nickel pyridine complexes are, therefore, formed in a single stage, and when their formation reaches a maximum equilibrium value, the absorption remains practically constant.

It is intended to make a systematic and quantitative study of infrared absorption by solutions of inorganic substances with a view to determine the nature of the molecule responsible for the absorption.

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FIG. 3. Change in absorption of various copper solutions upon the addition of the reagents shown.

The Location of the Activator in Fluorescent ZnS–Cu

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IN several papers evidence has been given for the view that ZnS phosphors prepared in the presence of halogen ions (Cl, Br, or I) take up an amount of halogen of the order of the concentration of the activator.[1,2] In a recent note Bube[3] has published results of a chlorine analysis of ZnS-Cu prepared with NaCl which support this view. There are differences, however, in the way in which this fact is explained.

According to Kröger et al.,[2] in green fluorescent ZnS-Cu the halogen is incorporated as a monovalent negative ion at a normal anion lattice site, thus making possible the simultaneous incorporation of the monovalent activator ion (Cu$^+$) at a normal cation lattice site. The charge compensation can also be accomplished