

In addition to a study and possible improvement in the conditions of flow back of the diaphragm, the further development of the method would also demand more reliable temperature measurements in the flowing gas. This could perhaps be achieved by using much finer thermocouple wire, sealed across the tube to provide the stiffness necessary to withstand the flow of gas.

In conclusion it may be remarked that the experiments which we have described are in any case of considerable interest, since they at least exhibit qualitatively a definite positive effect which can only be explained by a high rate of dissociation of nitrogen tetroxide, in contrast to the acoustic experiments which so far have led only to negative effects from which a high rate can be inferred.

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NOTES

A Simply Constructed Absolute Manometer.—This note describes a manometer developed in this Laboratory which we believe is unique if not superior to the usual types. It possesses the following features: (1) it may be constructed in almost any chemical laboratory; (2) it is easily emptied and cleaned; (3) the readings are absolute; (4) at least fair accuracy may be obtained without "boiling out" with mercury.

The construction is obvious from the drawing. If a cathetometer is not used, a scale is to be fixed between or in back of the second and third tubes which comprise the manometer proper. With the system open there will be about 29 inches between the upper and lower levels, so enough extra length is necessary to care for oscillations of the column after opening the system. The short arm at the left should be slanted considerably for reasons discussed later. Fairly large tubing is preferable to the usual barometer tubing since the error due to differences in capillarity when the walls become slightly dirty is practically eliminated. Six millimeter tubing is not too large. The tubes accessory to the manometer may be smaller to conserve mercury.

Mounting.—A board serves well to hold the tubes, which may be secured by fine wires. The greater the distance between the manometer tubes the greater the error if they are not perpendicular. This is not true, of course, if a cathetometer is used.

Filling.—The instrument is ready for use when the levels are conveniently adjusted and the space T is void of air. Use the best mercury obtainable, place the mounted instrument horizontally with the left side downward, immerse tube A in the mercury and apply a gentle, easily controlled vacuum to the other end. By proper manipulation of the instru-

ment and vacuum the mercury will rise, completely filling the tube until a point near 4 is reached. Close the stopcock, disconnect the vacuum and bring the instrument slowly to a vertical position. Excess mercury in the short arm may be poured out easily if the stopcock plug is withdrawn.

Unless such a device is "boiled out" with mercury, adsorbed air on the glass will eventually collect in space T. It may be detected by tipping the manometer backward. If air is present a minute bubble will persist after the columns should have connected. This bubble may be removed as follows. Connect both ends of the manometer to the same vacuum system. With a slight reduction of pressure draw level 1 just to the stopcock, which is then closed. Tip the instrument to the left to a horizontal position as when filling. If level 4 was originally high enough relative to the volume of T, no air will be admitted around the last bend. Set the slope of the tubes so that the bubble will just rise and escape near 4. Increasing the vacuum and tapping will aid in moving the bubble. Any air trapped in the recesses of the stopcock will not get past the first bend. Leakage at the stopcock is prevented by having the same vacuum attached at both ends. If the mercury can be kept clean this apparatus can be used with increasing accuracy. For rough work where the mercury is quickly dirtied, cleaning is much easier than in the case of the closed type since cleaning fluid and the like can be drawn or poured through without the fussy technique required by the latter.

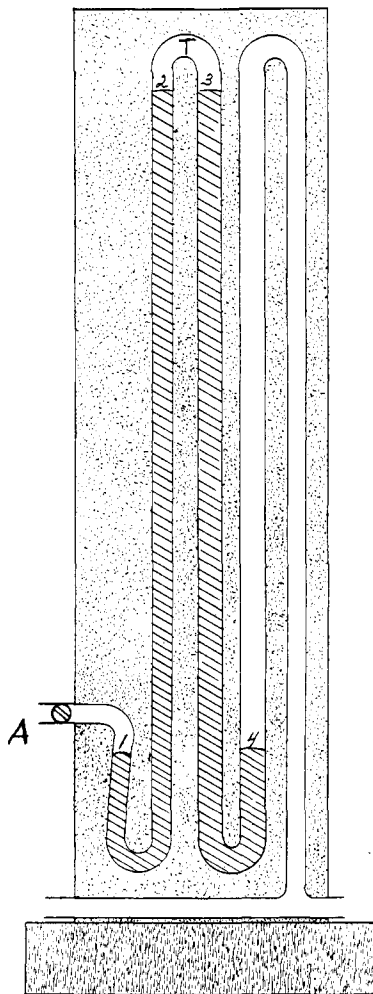


Fig. 1.

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Some Observations on Reactions between Certain Metallic Ions and the Ammonium Salt of Aurintricarboxylic Acid.—Several years ago Hammett and Sottery¹ discovered that the ammonium salt of aurintricarboxylic acid could be used as a very sensitive reagent for the detection of aluminum. The new reagent is called "Aluminon." In acetic acid-acetate solution aluminum forms a bright red lake with this dye, which is fairly stable in ammonium hydroxide—ammonium carbonate solution. Observations on most of the common metallic ions, as well as silicic acid and phosphate, were made with this reagent. Ferric iron was the only one found to give a colored precipitate, the others either gave white precipitates or none at all. Iron, therefore, must be completely removed from the aluminum. This may be accomplished by co-precipitation of the iron with relatively large amounts of elements such as copper. Precipitation with sodium hydroxide, or sodium sulfide, followed by digestion for thirty to sixty minutes on a steam-bath, is satisfactory.

Middleton² reports that "Aluminon" forms lakes with the hydroxides or basic acetates of beryllium, cerium, erbium, lanthanum, neodymium, thorium, yttrium and zirconium. These lakes are deeper red than the aluminum lake but all, except that of beryllium, are either dissolved or decolorized by ammonium carbonate.

Corey and Rogers³ have studied the reactions of "Aluminon" with gallium, germanium, indium, scandium and thallium. With the exception of germanium, these elements form red lakes, but they are destroyed by ammonia or ammonium carbonate solutions.

Lundell and Knowles⁴ made use of the "Aluminon" reagent in the quantitative determination of small amounts of aluminum in non-ferrous alloys.

Yoe and Hill⁵ made an extensive study of the various factors involved in the use of this reagent and developed a method for the colorimetric determination of aluminum in potable water. The method is also applicable to the determination of small quantities of aluminum in salts, minerals, rocks, etc.

In this note we report further studies with "Aluminon." Observations with nineteen elements, most of them rare elements, have been made. In most cases the chloride or nitrate was used; in a few instances the sulfate or oxalate. The concentration of the metallic ion was approximately twenty parts per million in the final dilution, *i. e.*, 0.24 mg. per 12 ml. The "Aluminon" reagent was 0.1% in water solution.

The following procedure was observed. To a measured amount of a given salt the reagents were added in the order listed: (1) 2 ml. of 1 *N* HCl; (2) 2 ml. 3 *N* NH₄Ac; (3) 2 ml. "Aluminon," allowed to stand five to

¹ Hammett and Sottery, *THIS JOURNAL*, **47**, 142 (1925).

² Middleton, *ibid.*, **48**, 2125 (1926).

³ Corey and Rogers, *ibid.*, **49**, 216 (1927).

⁴ Lundell and Knowles, *Ind. Eng. Chem.*, **18**, 60 (1926).

⁵ Yoe and Hill, *THIS JOURNAL*, **49**, 2395 (1927).

ten minutes; (4) 2 ml. 6 *N* NH₄OH; (5) 4 ml. 6 *N* (NH₄)₂CO₃. The results are recorded in the following table.

TABLE I
ANALYTICAL RESULTS

Ion	"Aluminon"	NH ₄ OH	(NH ₄) ₂ CO ₃
Arsenic, As ⁺⁺⁺	Red soln.	Almost decolorizes soln.	Decolorizes soln.
Columbium, Cb ⁺⁺	Brownish-red ppt.	Ppt. dissolves giving pale yellow soln.	Decolorizes soln.
Dysprosium, Dy ⁺⁺⁺	Red soln.	Purple soln.	Decolorizes soln.
Gadolinium, Gd ⁺⁺⁺	Red ppt.	Ppt. dissolves giving purple soln.	Decolorizes soln.
Hafnium, Hf ⁺⁺⁺⁺	Deep pink soln.	Light pink soln.	Decolorizes soln.
Iridium, Ir ⁺⁺⁺⁺	Red soln.	Pale yellow soln.	Soln. almost colorless
Molybdenum, ^a Mo ⁺⁺⁺⁺⁺	Red ppt.	Ppt. dissolves giving pale yellow soln.	Soln. almost colorless
Praseodymium, Pr ⁺⁺⁺	Red ppt.	Ppt. dissolves giving pink soln.	Decolorizes soln.
Rhenium ^b	Red soln.	Pale yellow soln.	Soln. almost colorless
Rhodium, Rh ⁺⁺⁺	Brownish-red ppt.	Ppt. dissolves giving pale yellow soln.	Soln. almost colorless
Ruthenium, Ru ⁺⁺⁺	Pink soln.	Pale yellow soln.	Dingy yellow soln.
Samarium, Sm ⁺⁺⁺	Red soln.	Pale purple soln.	Decolorizes soln.
Tantalum, Ta ⁺⁺⁺⁺⁺	Brownish-red ppt.	Ppt. dissolves giving pale yellow soln.	Soln. almost colorless
Tellurium, ^a Te ⁺⁺⁺⁺⁺	Red soln.	Pale yellow soln.	Soln. almost colorless
Thulium, Tm ⁺⁺⁺	Red soln.	Purple soln.	Decolorizes soln.
Tungsten, W ⁺⁺⁺⁺⁺	Brownish-red ppt.	Ppt. dissolves giving pale yellow soln.	Soln. almost colorless
Uranyl, (UO ₂) ⁺⁺	Red soln.	Pale yellow soln.	Soln. almost colorless
Vanadium, V ⁺⁺	Scarlet ppt. and soln.	Ppt. partly dissolved, soln. pale pink	Dissolves ppt.
Ytterbium, Y ⁺⁺⁺	Deep pink soln.	Pink soln.	Decolorizes soln.

^a The metal was dissolved in *aqua regia*. The ions are assumed to be in the highest state of oxidation.

^b The metal was treated with *aqua regia* and the mixture evaporated to dryness. Concentrated nitric acid was added to the residue and evaporated to dryness. This treatment was repeated and the residue taken up in distilled water.

An inspection of the table shows that gadolinium, molybdenum, praseodymium and vanadium give red precipitates. All are dissolved and decolorized by ammonia or ammonium carbonate. Columbium, rhodium, tantalum and tungsten give brownish-red precipitates soluble in ammonia and decolorized to a pale yellow. The remaining elements give red or deep pink solutions with "Aluminon," but all were decolorized by ammonia or ammonium carbonate. It is evident that none of the above elements will interfere with the detection of aluminum by the "Aluminon" reagent. Beryllium forms a lake similar to the aluminum lake and hence the reagent does not distinguish between these two elements.

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A Simple Derivation of General Equations of Energy and Entropy of Gases.—Recently the author,¹ by employing the characteristics of exact differentials, deduced general equations of energy and entropy of gases whose generalized equation of state is

$$p = T\Psi(v) - \Phi(v) - F(v, T) \quad (1)$$

While this method of derivation² is exact, it is rather time consuming. The author has now found that these equations can be directly and very easily deduced by using the following two thermodynamic formulas

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \quad (2)$$

$$\left(\frac{\partial u}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - p \quad (3)$$

For, from Equation 1, we have by differentiation at constant volume

$$\frac{\partial p}{\partial T} = \Psi(v) - \frac{\partial F}{\partial T} \quad (4)$$

Substituting Equation 4 into Equation 2 and integrating, we get

$$S = \int \Psi(v)dv - \int \frac{\partial F}{\partial T} dv + \beta(T) \quad (5)$$

which is the general equation of entropy. Substituting Equations 1 and 4 into Equation 3 and integrating, we get

$$u = \int \Phi(v)dv + \int \left[F - T \frac{\partial F}{\partial T} \right] dv + \alpha(T) \quad (6)$$

which is the general equation of energy. The general applicability of Equations 5 and 6 has already been shown.¹

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¹ Huang, *Phys. Rev.*, **37**, 1171 (1931).

² For the detail of derivation by the method of exact differentials see "Science Reports of National Tsinghua University," First Series, Vol. I, No. 3 (in press).