It is obvious that the X-ray method does not reveal the condition of the surface of the catalysts. By the process of elimination and in agreement with the generally accepted view, it must be concluded that the condition of the surface predominatingly determines activity.

Summary

1. Powder diffraction photographs in a new, inexpensive, but precise spectrograph have been taken of nickel catalysts of widely different hydrogenation and dehydrogenation activities, prepared by reduction with carbon, alcohol, ethyl acetate, hydrogen and sodium hypophosphite. Except for the last, which appeared colloidal, all give identical lines for nickel, d_{100} = 3.536 Å. Hence the difference in activities is not to be ascribed to a difference in lattice type or dimensions.

2. Precision photodensitometer curves from the films were prepared and used to measure relative intensities and widths of lines. The intensities for all were approximately the same and in fair agreement with the calculated values for a face-centered lattice.

3. The nickel catalysts do not obey the Debye-Scherrer equation connecting line width with particle size, defined for colloidal dimensions. A rough parallelism is found between decreasing line width and increasing catalytic activity.

4. X-rays give no information concerning the surface of catalysts.

5. Precision measurements on nickel monoxide (simple cubic) gave d_{100} = 4.16 Å. Nickel sesquioxide, Ni_2O_3, gave only the lines of the monoxide, proving it to be $NiO.NiO_2$. Photographs of the dioxide in its two forms gave no diffraction lines, explaining the non-appearance of these lines on the sesquioxide film. Nickelo-nickelic oxide, Ni_3O_4, was also amorphous.

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VANADIUM OXYTRICHLORIDE AS A SOLVENT

By F. E. Brown and J. E. Snyder

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Introduction

Lenher[1] has shown that selenium oxychloride is a remarkable solvent. It was thought that oxychlorides of other elements near selenium in the periodic table might also be good solvents. Vanadium oxytrichloride is liquid between —15° and +127.19°. It is light yellow, transparent and could be prepared in large quantities at a moderate cost. It may be refluxed over sodium for several days without suffering appreciable reduction or decomposition.

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[1] Lenher, This Journal, **43**, 29 (1921).

The only serious inconvenience in using it as a solvent is its tendency to hydrolyze. It dissolves traces of water, forming a red solution. A larger amount of water forms a red precipitate of vanadium pentoxide which may be dissolved by adding hydrochloric acid.[2]

Solubilities in vanadium oxytrichloride have been determined for only a few substances. Koppel and Kaufmann[3] report that it is soluble unchanged in alcohol and ether, but is insoluble in chloroform. Experiments in this Laboratory show that vanadium oxytrichloride and chloroform are miscible in all proportions.

Preparation of Vanadium Oxytrichloride

The vanadium oxytrichloride used in these experiments was prepared and purified by the method used by Briscoe and Little[4] when they prepared vanadium oxytrichloride for the determination of the atomic weight of vanadium. The liquid obtained in this manner was clear, lemon-colored and boiled between 124° and 125° (739 mm.).

Action on Elements

Small samples of the solid elements were dried and allowed to stand in about 5 cc. of vanadium oxytrichloride at room temperature for about 24 hours. When no action was apparent, the temperature of the solvent was raised to the boiling point.

Metals.—The following metals are apparently unaffected by the solvent, either at room temperature or at its boiling point: aluminum, arsenic, bismuth, copper, iron, manganese, nickel, platinum, potassium, sodium and tin.

Non-Metals.—Chlorine is very soluble at 0° but its solubility decreases rapidly as the temperature is raised. Bromine is miscible in all proportions at room temperature. Iodine is slightly soluble. Red phosphorus is insoluble. White phosphorus dissolves at room temperature without apparent reaction. Sulfur is soluble.

Action on Inorganic Compounds

Anhydrous.—A small crystal of each of the following compounds containing no water of crystallization and weighing less than 0.01 g., was dried over phosphorus pentoxide and then allowed to stand in 5 cc. of vanadium oxytrichloride at room temperature for 24 hours. The solvent was then heated to boiling. There was no evidence of reaction or solution in any case.

Aluminum chloride
Ammonium molybdate
Barium carbonate
Barium chloride
Barium nitrate
Barium sulfate
Bismuth chloride
Bismuth sulfate

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[2] Berzelius, *Pogg. Ann.*, **22,** 1 (1831).

[3] Koppel and Kaufmann, *Z. anorg. Chem.*, **45,** 352 (1905).

[4] Briscoe and Little, *J. Chem. Soc.*, **105,** 1310 (1914).

Cadmium bromide
Cadmium carbonate
Calcium carbonate
Calcium chloride
Ferric chloride
Lead nitrate
Lead sulfate
Phosphorus pentoxide
Potassium acetate
Potassium bromate
Potassium bromide
Potassium carbonate
Potassium chlorate
Potassium chloride
Potassium chromate
Potassium dichromate
Potassium ferricyanide
Potassium hydroxide
Potassium iodide
Potassium nitrate
Potassium perchlorate
Potassium permanganate
Potassium pyro-antimonate
Potassium pyrosulfate
Potassium sulfate
Potassium sulfate, acid
Potassium tartrate, acid
Potassium thiocyanate
Sodium acetate
Sodium arsenite
Sodium bromide
Sodium carbonate
Sodium chloride
Sodium hydroxide
Sodium iodide
Sodium nitrate
Sodium nitrite
Sodium sulfite
Strontium carbonate
Strontium nitrate
Strontium sulfate

Sulfuryl chloride is miscible in all proportions. Phosphorus oxychloride is also miscible in all proportions, but almost immediately reacts and forms a brown precipitate. Phosphorus trichloride reduces the vanadium oxytrichloride, forming a precipitate.

Compounds Containing Water of Crystallization.—Small crystals of the following compounds containing water of crystallization swell and blacken when boiled with the solvent. This is probably due to removal of water from the crystal and subsequent formation of an hydrolysis product of the oxytrichloride. There is no evidence of solubility.

Barium acetate
Barium chlorate
Barium hydroxide
Bismuth carbonate
Potassium alum
Potassium antimonyl tartrate
Potassium chrome alum
Potassium ferrocyanide
Potassium oxalate
Potassium sodium carbonate
Potassium sodium cobaltinitrite
Potassium sodium tartrate
Sodium ammonium hydrogen phosphate
Sodium arsenate, secondary
Sodium dichromate
Sodium phosphate, primary
Sodium phosphate, secondary
Sodium phosphate, tertiary
Sodium tartrate
Sodium tetraborate
Strontium acetate
Strontium chloride

Action on Organic Compounds

Hydrocarbons.—The following hydrocarbons are miscible in all proportions; they give red solutions: *n*-hexane, *n*-octane, benzene, toluene, petroleum ether, paraffin (when melted).

Commercial kerosene and gasoline dissolve and then react, giving murky mixtures. Naphthalene and paraffin are soluble.

Halogen Substitution Products.—The following halogen substitution compounds are miscible in all proportions: carbon tetrachloride, chloroform, ethyl bromide, ethyl chloride, ethyl iodide, *iso*-amyl bromide.

Aldehydes.—The following liquid aldehydes react vigorously at room temperature giving insoluble products: anisic aldehyde, benzaldehyde, *n*-butyraldehyde, cinnamic aldehyde, *n*-heptaldehyde, salicylic aldehyde. β-Hydroxybenzaldehyde and *o*-nitrobenzaldehyde, both solid, are soluble but not reactive.

Other Compounds.—Acetone and acetic anhydride are miscible in all proportions and reactive. Ethyl alcohol is miscible in all proportions, and non-reactive. Benzophenone is soluble and non-reactive.

Quantitative Solubility of Sulfur

An excess of dried, powdered sulfur was added to a sample of vanadium oxytrichloride and the mixture was placed in a constant-temperature oil-bath. When equilibrium was reached, the excess of sulfur was removed by filtering at constant temperature in a dry atmosphere. This was accomplished by using a filtering apparatus enclosed in a jar which was completely submerged in the same bath. After the solution had been weighed, the solvent was decomposed by means of water and hydrochloric acid. The precipitated sulfur was washed, dried, crystallized from carbon disulfide, dried and weighed. The results are given in Table I.

TABLE I

SOLUBILITY OF SULFUR

Temp., ° C.	Wt. of S dissolved in 100 g. of $VOCl_3$, g. 1	2	3	Mean
0	3.33	3.30	3.29	3.307
20	5.93	6.06	...	5.995
45	12.99	13.21	13.11	13.103
65	31.7	30.7	29.8	30.73

At temperatures above 80° sulfur is very soluble and the solution becomes viscous. After a time, the mixture solidifies and the odor of sulfur dioxide mixed with that of a volatile vanadium compound is quite noticeable. The following reaction probably takes place:[5] $2VOCl_3 + S \longrightarrow 2VCl_3 + SO_2$.

Summary

Vanadium oxytrichloride was prepared and purified.

The solubilities in it of about 125 substances were tested. It was found that of these, (1) nearly all of the inorganic compounds were insoluble; (2) most of the non-metals were soluble; (3) the metals were unaffected; (4) all of the purely organic compounds either dissolved, reacted, or both; (5) the organic liquids were miscible in all proportions; (6) the liquid alde-

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[5] Ruff and Lickfett, *Ber.*, **44**, 509 (1911).

hydes reacted vigorously. The solubility of sulfur was determined quantitatively for temperatures between 0° and 65°.

AMES, IOWA

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE CHEMICAL ACTION OF GASEOUS IONS PRODUCED BY ALPHA PARTICLES.[1] VI.[2] REACTIONS OF THE OXIDES OF CARBON

BY S. C. LIND AND D. C. BARDWELL

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In 1912 one of us collected the data[3] on chemical reaction under the influence of α-radiation and found close equivalence between the number of molecules (M) reacting chemically and the number of ions (N). Although the data were not sufficiently accurate to establish exact reaction mechanisms, it was sought to generalize the principle discovered into a modified form of Faraday's law applying to gaseous ions,[4] while still recognizing that, owing to the variety of the latter, the gaseous-ionic would not necessarily be identical with the electrolytic equivalents. This principle of equivalence was questioned by Debierne[5] and Wourtzel[6] on account of their experiments showing that *two* or *three* molecules of hydrogen sulfide, nitrous oxide or ammonia gas are decomposed for each ion pair instead of only *one* molecule of each.

If it were true that each molecule ionized by an α-particle decomposed directly, then $-M/N = 1$ would be expected. The results, however, of later work by the writers, including the present and subsequent papers, show that the first step is one of addition of neutral molecules to the ions and not of decomposition of the latter. Even when decomposition is the final result, it takes place through intermediate formation of an ion-addition product. There are, then, at least two processes by which the M/N ratio is multiplied a few fold beyond unity. Consequently, the values of $M/N > 1$, instead of disproving the *ionic* nature of the reaction,

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[1] Published with permission of the Director of the Bureau of Mines.

[2] The five preceding papers [THIS JOURNAL, **41**, 531, 551 (1919); **45**, 2585, 2593 (1923); **46**, 2003 (1924)], which will be referred to as Part I, Part II, etc., were published under the general title "Chemical Action Produced by Radon." The series is now continued under a changed title to lay stress on *ionization* as a mode of chemical activation, rather than on radon as the agency which happens to afford the most convenient means of obtaining ionization in known quantity.

[3] Lind, *J. Phys. Chem.*, **16**, 564 (1912).

[4] Lind, *Le Radium*, **9**, 426 (1912); *Z. physik. Chem.*, **84**, 759 (1913).

[5] Debierne, *Ann. phys.*, [9] **2**, 97 (1914).

[6] Wourtzel, *Compt. rend.*, **157**, 929 (1913); *Le Radium*, **11**, 289, 332 (1919); *J. Phys. Rad.*, **1**, 77 (1920); **2**, 53 (1921).