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A CORRELATION OF THE CATALYTIC ACTIVITY OF VARIOUS MIXTURES OF RHENIUM AND MOLYBDENUM SULFIDES IN LIQUID-PHASE HYDROGENATION OF CERTAIN REDUCIBLE ORGANIC GROUPS

A Thesis

by

Li-Chen Hsu

B.S. in Chemical Engineering

Chinese National University of Chekiang

1942

Submitted in Partial Fulfillment

of the Requirements for the Degree of

Master of Science in Chemistry

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Provo, Utah

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This thesis by Li-Chen Hsu is accepted in its present form by the Department of Chemistry and Chemical Engineering of the Brigham Young University as satisfying the thesis requirement for the degree of Master of Science.

Signed

6/12/56
Date

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The writer wishes to express his deep indebtedness to Dr. H. Smith Broadbent for his earnest and valuable advice.

The writer also would like to take this opportunity to express his gratitude to Professor Joseph K. Nicholes and Mr. Gordon P. K. Chu; through their kind help and encouragement he was able to advance his studies in the United States especially at such a fine school as the Brigham Young University.

Finally, acknowledgment is made to the Kennecott Copper Corporation, which provided financial aid to the writer by way of a research fellowship.

DEDICATION

This thesis is dedicated by the writer to his parents, Mr. and Mrs. Berming Hsu, and also to his former college adviser, Dr. Kung Vie, Professor of Economics at the Chinese National University of Chekiang.

TABLE OF CONTENTS

Page

LIST OF TABLES

Table | Page

Table Page

Figure Page

I. INTRODUCTION

When a second component is added to a one-component catalyst for a chemical reaction, a large number of different consequences may arise. If the added substance has itself little catalytic effect toward the same chemical reaction, the possible consequences are shown by the curves in Fig. 1, in which A is the original catalyst of certain catalytic activity and B is the added substance of relatively inert or of zero activity by itself.

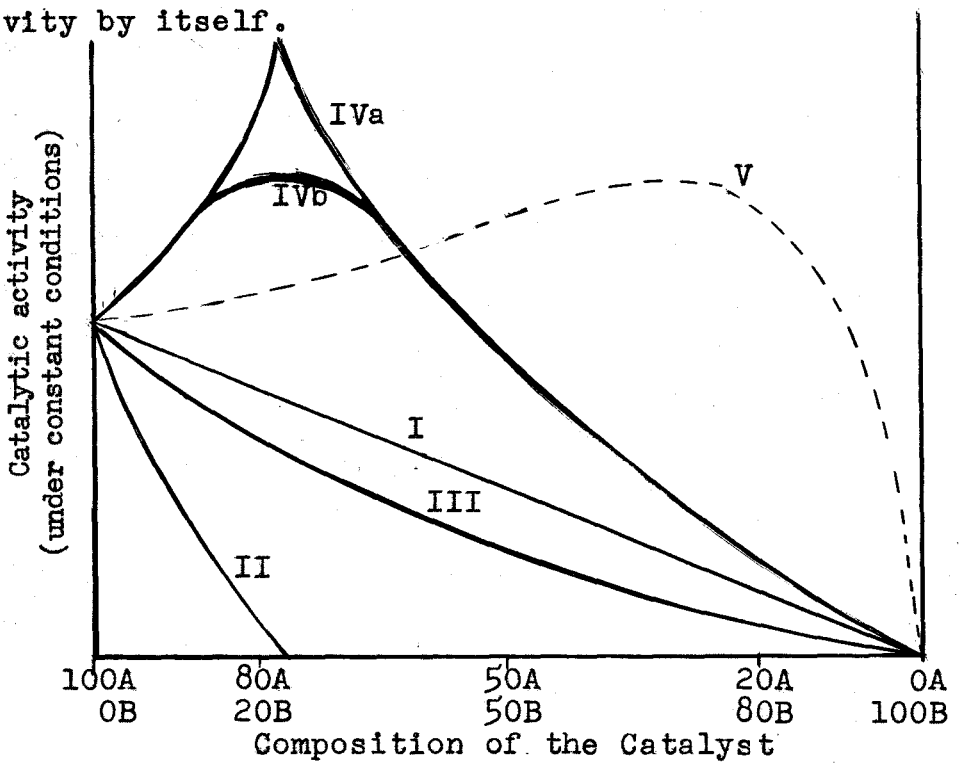

Fig. 1.--Possible Consequences of Mixing Catalysts wherein the Added Substance Is Relatively Inert toward the Given Chemical Reaction.

Curve I shows the simplest consequence in which straight dilution occurs.

Curve II shows A is poisoned by B.

Curve III shows A is deactivated by B.

Curve IVa or IVb shows the promoter action of B on A (simple activation); usually the curve rises to a very sharp maximum and then falls steeply again, as IVa.

Curve V shows the support effect in which the increase of catalytic activity is simply due to the increase of the active surface area of A through the dispersion on the carrier B.

The curves in Fig. 2 show the possible consequences of mixing catalysts wherein the added substance B is also a catalyst toward the given chemical reaction.

Curve I shows that their combined effect is the same as if each were reacting singly.

Curve II shows that A is poisoned by B.

Curve III shows that their joint effect is smaller than the sum of their individual activities. Each is deactivated by the other.

Curve IVa or IVb shows the co-activation of A and B. Each is promoted by the other.

Quantitatively, the curves in both Fig. 1 and Fig. 2 are arbitrarily drawn. However, they may represent the various possibilities for modifications of catalyst activities in two component systems. Among those consequences, only the promoter action, either simple activation or co-activation, is considered to be valuable.

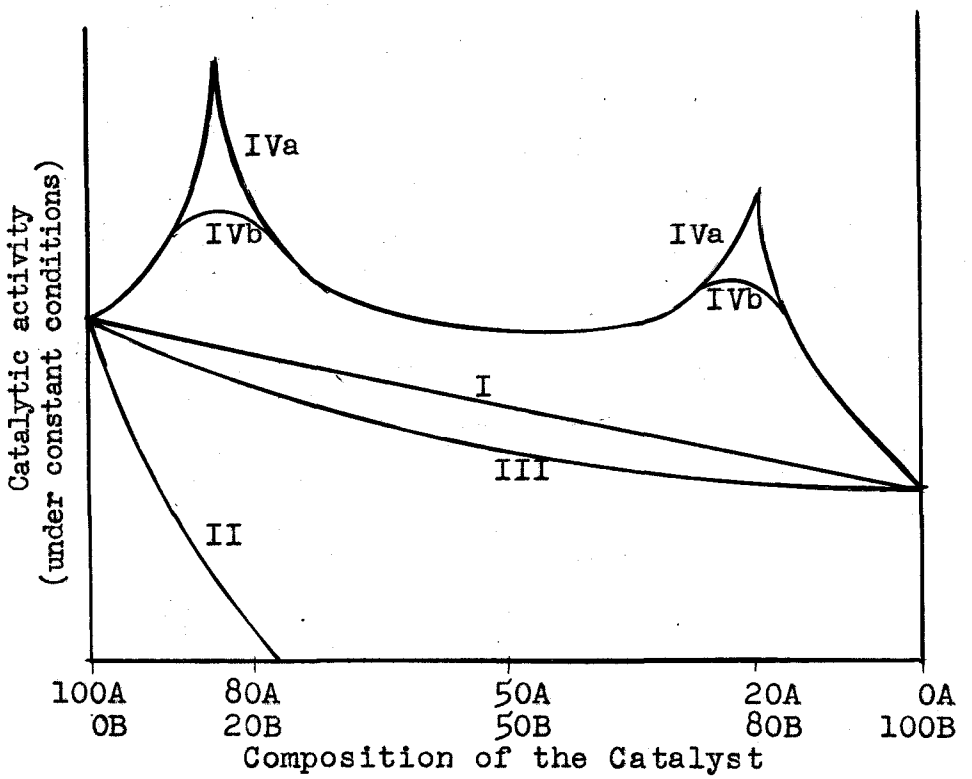

Fig. 2.--Possible Consequences of Mixing Catalysts wherein the Added Substance Is Also a Catalyst toward the Given Chemical Reaction.

Pease and Taylor[1] define promoter action as including "all those cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the supposition that each substance in the mixture acts independently and in proportion to the amount present."

The case of supporting effect fits this definition. However, strictly speaking, it should not be considered as promoter action. The increase of catalytic activity is merely

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[1]Pease and Taylor, J. Phys. Chem., 24, 241 (1920) /Ellis, "Hydrogenation of Organic Substances," 3rd ed., D. Van Nostrand Co., New York, 1930, p. 527/.

due to the increase of the active surface area of A through the dispersion of B.

The promoter action of multicomponent[2] (or mixed[3] or combined[4]) catalysts has been systematically studied since about 1900. Some of them in the field of catalytic hydrogenation will be cited in the following chapter.

Since the catalytic properties of molybdenum sulfide and of rhenium heptasulfide in liquid-phase hydrogenation of various reducible organic compounds have been investigated by Dr. H. Smith Broadbent[5] and his students in the Brigham Young University chemistry research laboratory, it seemed advisable to make a further study on the catalytic activity of mixtures of molybdenum sulfide, the most well-known sulfide catalyst, and rhenium heptasulfide, which is reported so far as the best sulfide catalyst in hydrogenation.[5]

In this study:

(1) Mixtures of rhenium and molybdenum sulfides in different proportions (as well as pure rhenium sulfide and pure molybdenum sulfide) were prepared by co-precipitation

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[2]Frankenburg, Komarewsky, and Rideal, "Advances in Catalysis and Related Subjects," Academic Press, New York, 1950, Vol. II, p. 52.

[3]Rideal and Taylor, "Catalysis in Theory and Practice," Macmillan & Co., London, 1926, p. 100; Ellis, op. cit., p. 54.

[4]Brode, J. Chem. Z., 24, 1116 (1901); Z. Physik. Chem., 37, 257, 290 (1901); ibid., 49, 209 (1904) /Frankenburg, Komarewsky, and Rideal, op. cit., p. 82/.

[5]Broadbent, H. Smith; Slaugh, Lynn H.; and Jarvis, N. Lynn, J. Am. Chem. Soc., 76, 1519 (1954).

from potassium or ammonium perrhenate and ammonium molybate with hydrogen sulfide in hydrochloric acid solutions of different concentrations, in ammonium hydroxide solutions of different concentrations, and by co-precipitation with sodium thiosulfate in dilute sulfuric acid solution.

(2) The mixtures of sulfides prepared were analyzed to ascertain whether the mixtures of rhenium and molybdenum sulfides prepared from given concentrations of potassium or ammonium perrhenate and ammonium molybdate under different conditions had the same composition.

(3) The mixtures of sulfides prepared were then used as catalysts in hydrogenation of nitrobenzene, styrene, and cyclohexanone with the following objects in mind: (a) determining whether the mixtures of rhenium and molybdenum sulfides of a given composition but prepared under different conditions would possess different catalytic hydrogenation properties toward the nitro group, the carbon-carbon double bond conjugated with benzene ring, and the carbon-oxygen double bond, and (b) correlating the relative proportions of the two sulfides in a series of catalyst mixtures prepared under known sets of conditions with their catalytic activity toward the double bonds mentioned in (a).

II. LITERATURE REVIEW

A. Molybdenum Sulfides

1. Molybdenum Disulfide, MoS_2. Molybdenite, the chief ore of molybdenum, is the natural form of molybdenum disulfide. Pure MoS_2 can be prepared from its elements from the reaction of the trioxide with H_2S, with sulfur and potassium carbonate,[6] with sodium sulfide,[7] or from heating[8] or reduction[9] of the trisulfide.

The structure of MoS_2 is shown in Fig.3. It consists of a layer lattice with hexagonal symmetry. Each Mo atom has 6 S atoms at the points of a trigonal prism; the distances are Mo-S 2.35, Mo-Mo 3.15, S-S 3.08, X10^{-8} cm.[10] Slippage along the planes of the weak S-S bonds is reported to be responsible for its greasy feel and its lubricating properties.[11]

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[6]Sidgwick, "The Chemical Elements and Their Compounds," Clarendon Press, Oxford, 1950, Vol. II, p. 1055.

[7]Polozov and Feofilov, Novosti Tekhnike, 36, 20 (1936) /C. A., 31, 2757 (1937)/.

[8]Biltz and Köcher, Z. anorg. Chem., 248, 172 (1941) /Sidgwick, op. cit., p. 1038/.

[9]Balger, Griffith, and Newling, Proc. Roy. Soc. (London), A197, 184-93 (1949) /C. A., 44, 2357 (1950)/.

[10]Dikinson and Pauling, J. Am. Chem. Soc., 45, 1466 (1923); Hassel, Z. Krist., 61, 92 (1925) /Sidgwick, op. cit., p. 1055/.

[11]Hampel, "Rare Metals Handbook," Reinhold Publishing Corp., New York, 1954, p. 281.

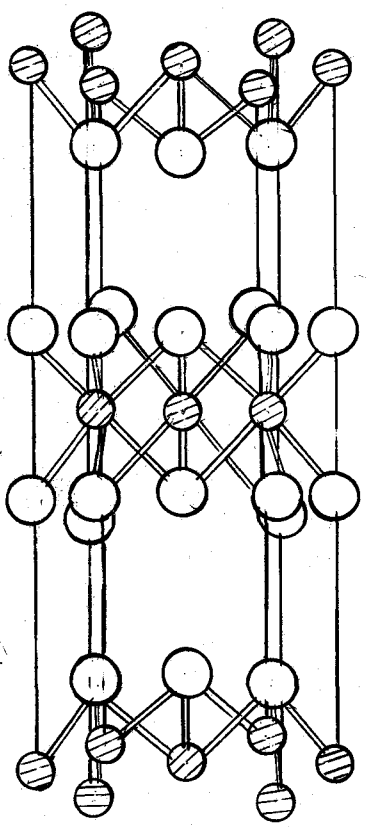

Fig. 3.--The MoS_2 Crystal, Showing Incomplete Cells with Molybdenum Layers Exposed.

Mo S

It has a metallic conductivity at any rate above 200°C.[12] Its thermochemical properties, calculated from measuring the E.M.F. of a cell by Makolkin,[13] are as follows:

$$\Delta F^{\circ}_{298k} = -53.96 \text{ Kcal}$$

$$\Delta H^{\circ}_{298k} = -55.93 \text{ Kcal}$$

$$S^{\circ}_{298k} = 15.46 \text{ E.U.}$$

On heating it decomposes to S and Mo.[14]

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[12]Tubandt and Haedicke, Z. anorg. Chem., 160, 306 (1927) /Sidgwick, op. cit., p. 1055/.

[13]Makolkin, J. Phys. Chem. (U.S.S.R.), 14, 110-12 (1940) /C. A. 35, 959 (1941)/.

[14]Parravano and Malguori, Atti. R. Linc. (Vi) 7, 109 (1928) /Sidgwick, op. cit., p. 1055/.

2. Molybdenum Trisulfide, MoS_3. Molybdenum trisulfide cannot be made from its elements or by the reaction of MoS_2 and S.[8] It can be prepared by saturating H_2S from the hydrochloric or sulfuric acid solution of a molybdate, from the aqueous or ammonium hydroxide solution of a molybdate followed by acidifying with hydrochloric or sulfuric acid. In the latter case, the precipitate easily goes over into a colloidal form. It can also be precipitated from thio compounds with acid.[15]

It is a dark brown solid. It is soluble in alkalies with which it forms the thiomolybdates. Its thermochemical properties are reported[16] as

$\Delta F^\circ_{298k} = -57.38$ Kcal $\qquad \Delta H^\circ_{298k} = -61.2$ Kcal

$S^\circ_{298k} = 16.88$ E.U.[17]

On heating it changes irreversibly into MoS_2 and S.[8]

3. Other Sulfides. Molybdenum persulfide, MoS_4, can be made by the action of H_2S in excess (probably under pressure) on a molybdate solution.[18] It is a brown powder like trisulfide.

Molybdenum pentasulfide, Mo_2S_5, is prepared by reducing a solution of ammonium molybdate in 20% sulfuric acid with

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[15]Standard I. G. Co., Ger. Patent 703,736, Feb. 13 (1941) [C. A., 36, 249 (1942)]

[16]Lange, "Handbook of Chemistry," 8th ed., Handbook Publishers, Ohio, 1952, p. 1644.

[17]S° of MoS_3 calculated by author from the equation $MoS_3 \rightarrow MoS + S$ and the data given for MoS_3 and MoS_2. S°_{298k} of sulfur is taken as 7.62 E.U. (rhombic).

[18]Sidgwick, op. cit., p. 1038.

zinc until it is wine-red, and then saturating it with H_2S. The dark brown precipitate of $Mo_2S_5.3H_2O$ loses its water if carefully heated to CO_2.[19]

Molybdenum sesquisulfide Mo_2S_3 can be prepared by heating the disulfide in an electric furnace either alone or mixed with lime and calcium fluoride.[20] It consists of steel-grey needles.

B. Rhenium Sulfides

The only stable sulfides of rhenium are rhenium heptasulfide and disulfide.

1. Rhenium Heptasulfide, Re_2S_7. It can be prepared by saturation with H_2S of an acid solution[21] of a perrhenate, or from an ammonical solution[22] of a perrhenate, then further followed by acidification with hydrochloric acid in order to complete the precipitation. It can also be precipitated by boiling a perrhenate with an excess sodium thiosulfate solution in presence of sulfuric acid (2-7 N) or hydrochloric acid (1-4 N).[23] All the above precipitates are in the form of hydrate $Re_2S_7.H_2O$ which may be dehydrated without loss of

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[19]Mawrow and Nikolow, Z. anorg. Chem., 95, 191 (1916) /Sidgwick, op. cit., p. 1049/.

[20]Muthmann and Mai, Ann., 355, 111 (1907) /Sidgwick, op. cit., p. 1058/.

[21]Briscoe, Robinson, and Rudge, J. Chem. Soc., 1932, 2673.

[22]Müller and La Lande, J. Am. Chem. Soc., 55, 2376 (1933).

[23]Geilmann and Bode, Z. anal. Chem., 130, 222-32 (1950) /C. A., 44, 4822 (1950)/.

sulfur by being heated in a high vacuum over phosphorous pentoxide, first to 140°C and then for a longer period (60 hours) to 160-170°C.[24]

The anhydrous heptasulfide can be directly obtained from the action of H_2S on dry Re_2O_7. It is a fine black amorphous powder easily oxidized by air, sometimes with incandescence. It begins to dissociate below its melting point and readily decomposes with evolution of heat into ReS_2 and free sulfur. Owing to its fine state of division, it is a powerful absorbent. It is not attacked by K_2S, HCl, or H_2SO_4, but it is oxidized to perrhenic acid by HNO_3, bromine water, or H_2O_2 in alkaline solution.

2. Rhenium Disulfide, ReS_2. Rhenium disulfide has been prepared by heating the heptasulfide to 350-400°C under a stream of inert gas such as CO_2,[5] by heating metallic rhenium to a red heat with an excess of sulfur in an atmosphere of hydrogen sulfide,[25] by heating the calculated quantities of the metal and sulfur to 1000°C in a sealed silica tube,[26] or by the action of H_2S on a solution of a tetravalent rhenium compound.[27]

It is a soft black substance with a structure like

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[24]Maxted, "Modern Advances in Inorganic Chemistry," Clarendon Press, Oxford, 1947, p. 192.

[25]Briscoe, Robinson, and Stoddart, J. Chem. Soc., 1931, 1439 /Sidgwick, op. cit., p. 1307/.

[26]Juza and Biltz, Z. Elektrochem., 37, 498 (1931) /Maxted, op. cit., p. 191/.

[27]Sidgwick, op. cit., p. 1307.

that of MoS_2.[28] It is a very stable substance which has an appreciable vapour pressure at temperatures above 1,000°C (13 mm at 1,110°C) and sublimes unchanged. Its heat of formation at 25°C is reported to be -44.3 Kcal.[29] It is insoluble in hydrochloric acid, sulfuric acid, alkaline hydroxide or sulfide solution; it can be oxidized to perrhenic acid.

C. Catalytic Hydrogenation

Catalytic hydrogenation is defined by Adkins and Shriner[30] as the addition of molecular hydrogen to a double or triple bond in the presence of a catalyst.

The difference between hydrogenation and reduction, or hydrogenation and hydrogenolysis, may be explained with the following diagram:

Reduction of organic compounds:

- (I) Gas-phase reduction....By molecular hydrogen
  - (1) Hydrogenation....Addition to a double or triple bond
  - (2) Hydrogenolysis...With the cleavage of a molecule
- (II) Chemical reduction.....By chemical reducing agent
- (III) Electrolytic reduction..By electrolysis

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[28]Lagrenaudie, J. Phys. Radium, 15, 299-300 (1954) [C. A., 48, 13399 (1954)].

[29]Lange, op. cit., p. 1602.

[30]Gilman, "Organic Chemistry, An Advanced Treatise," 2d ed., John Wiley & Sons, Inc., New York, 1953, Vol. I, p. 780.

1. The Role of the Catalyst in Hydrogenation

A catalyst accelerates a chemical reaction accompanied by a decrease of free energy under a given set of conditions to attain thermodynamic equilibrium (a minimum of free energy). Thus the role of the catalyst is

(a) To absorb and activate both hydrogen and the hydrogen acceptor,

(b) To hold them in the proper ratio and space relationship to allow for the addition of hydrogen to the molecule of the hydrogen acceptor, and

(c) To desorb the reduced compound.

The commonly accepted picture of the surface of the catalyst is one in which active centers presumably consist of atoms whose valence forces are not entirely satisfied by other atoms in the surface. Therefore, when hydrogen and a suitable hydrogen acceptor like carbon to carbon double bond come near the activated spots, they are attracted and adsorbed onto the surface of the catalyst and become activated. When they are held in the proper ratio and space relationship, a reaction between hydrogen and the unsaturated bond occurs, breaking the old bonds and forming new ones.

2. Factors Affecting the Rate of Hydrogenation

(a) Substrates or hydrogen acceptors. Various functional groups such as $>C=C<$, $-C\equiv C-$, $>C=N-$, $-C\equiv N$, $>C=O$, $-N^{+}\!<\!{}^{O^{-}}_{O}$, etc., can undergo catalytic hydrogenation. The rate of hydrogenation and the severity of conditions required depend on the structure (or the bond energy) of each of the individual

groups and also of its substituted groups. A few common groups are mentioned below for comparison.

The nitro group undergoes catalytic hydrogenation with great ease. The reaction is highly exothermic and caution must be taken to avoid excessively high temperatures. Both aromatic and aliphatic nitro compounds are readily reduced to the corresponding amines, and an alcoholic solution is ordinarily used in order to maintain the homogeneity of the solution even after all the oxygen of the nitro group has been converted to water. The free energy change and heat of reaction (both at 25°C) of the hydrogenation of nitrobenzene in aniline are calculated as follows:

$$C_6H_5NO_2\ (l) + 3\ H_2(g) \rightarrow C_6H_5NH_2\ (l) + 2\ H_2O_{(l)}$$

ΔF°_{298k}(Kcal)	33.90[31]	0	35.40	2 x-56.70
ΔH°_{298k}(Kcal)	2.68[31]	0	7.34	2 x-68.32

$$\Delta F = 35.40 + 2x\text{-}56.70 - 33.90 - 0 = -111.9 \text{ Kcal}$$

$$\Delta H = 7.34 + 2x\text{-}68.32 - 2.68 - 0 = -131.98 \text{ Kcal}$$

The carbon to carbon double bond is another easily reduced group. Almost 99% of all the known compounds containing the alkene linkage will add hydrogen at temperatures from 0°C to 275°C. The rate of hydrogenation and the severity of conditions required vary with substitution at the alkene carbons. Catalytic hydrogen adds most rapidly to isolated double bonds, less so to open chain conjugated double bonds, and least of all to the conjugated double bonds present in aromatic ring

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[31]Parks, J. Am. Chem. Soc., 58, 398 (1936).

systems. The free energy change and heat of reaction of the hydrogenation of styrene to ethylbenzene are calculated, for example, as follows:

$$C_6H_5CHCH_2(l) + H_2(g) \rightarrow C_6H_5CH_2CH_3\ (l)$$

ΔF°_{298k}(Kcal)[32]	51.10	0	28.61
ΔH°_{298k}(Kcal)[32]	24.72 (ca.)	0	-2.98

$$\Delta F_{298k} = 28.61 - 51.10 - 0 = -22.49 \text{ Kcal}$$

$$\Delta H_{298k} = -2.98 - 24.72 - 0 = -27.7 \text{ Kcal}$$

The carbonyl groups are considered a little harder to reduce than the nitro and alkene groups. The carbonyl group of ketones is reduced more slowly at room temperature over platinum and palladium catalysts than in the case of aldehydes. If the carbonyl group is attached to a benzene nucleus, the same care must be taken as with the aldehydes to prevent the first-formed secondary alcohol group being converted to a methylene group. If the carbonyl group is attached to a pyrrole nucleus it has proved impossible to stop the hydrogenation of the carbonyl at the carbinol stage. The catalytic hydrogenation of ketones is a process in which side reactions are seldom encountered, and the yields of secondary alcohols obtained are well above 90% for simple aliphatic ketones and 70-80% for the aryl ketones.

Some of the data for the catalytic hydrogenation of

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[32]Dreisbach, "Physical Properties of Chemical Substances," The Dow Chemical Co., 1952, Serial No. 1.3 & 2.1; Lange, op. cit., pp. 1671-86.

nitrobenzene, styrene, and cyclohexanone with different catalysts are summarized in Table 1.

(b) Catalysts. The chemical nature of a catalyst is naturally of importance; however, at the moment, it is not fully possible to predict the best catalyst for a hitherto unexplored reaction.

A high ratio of catalyst to hydrogen acceptor (100-150% by weight) is effective in lowering the temperature of reaction with hydrogen and makes possible certain hydrogenations which do not take place otherwise.[36]

The rate of hydrogenation is also dependent on the amount of available active surface area per unit mass (specific surface) of the catalyst. Therefore, the catalyst must be either finely divided or a very porous material. One method often used to increase the surface area is to disperse the catalyst on a carrier.

(c) Solvents. The solvent or reaction medium as well as the hydrogen, hydrogen acceptor and product, is no doubt adsorbed by the catalyst and so may play a role in determining the extent or course of the reactions. The solvent may be beneficial only because it facilitates the dispersion of the catalyst and the contact of the three essential materials, i.e., hydrogen, catalyst, and hydrogen acceptor. However, in some cases, a more special role is played by the solvent.[37]

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[36]Fuson, "Advanced Organic Chemistry," John Wiley & Sons, Inc., London, 1953, p. 259.

[37]Gilman, op. cit., p. 797.

TABLE 1

A Comparison of Catalytic Hydrogenations of Nitro Group (nitrobenzene), the Carbon to Carbon Double Bond Conjugated with Benzene Ring (styrene), and the Carbon to Oxygen Double Bond (cyclohexanone)

Catalyst* (g/mole of substrate)	Substrate*	Solvent*	Av.Temp. °C	Av.Pres. psi	Time hrs.	% Yield	Product*	Reference
PtO_2, 2.0	$PhNO_2$	EtOH	25	45	0.25	100	$PhNH_2$	33
PtO_2, 1.0	$PhCHCH_2$	EtOH	25	58	0.25	100	$PhCH_2CH_3$	34
PtO_2, 1.13	Cy=O	none	21	56	5.0	91	Cy-OH	35
Ni,	$PhNO_2$	EtOH	25	15	0.25	100	$PhNH_2$	35?
Ni, 3.0	$PhCHCH_2$	none	30	56	1.0	100	$PhCH_2CH_3$	35
Ni, 3.0	Cy=O	none	60	60	3.0	92	Cy-OH	35
$CuO.CuCr_2O_4$ (8.0)	$PhNO_2$	none	205	2400	1.5	98	$PhNH_2$	35
"	$PhCHCH_2$	none	122	2150	0.16	82	$PhCH_2CH_3$	35
"	Cy=O	none	115	2200	0.25	94	Cy-OH	35
MoS_2-3, 2.5	$PhNO_2$	EtOH	120	2300	2.5	0	$PhNH_2$	5
" "	$PhCHCH_2$	none	120	2000	3.0	8	$PhCH_2CH_3$	5

TABLE 1--Continued

Catalyst* (g/mole of substrate)	Substrate*	Solvent*	Av.Temp. °C	Av.Pres. psi	Time hrs.	% Yield	Product*	Reference
CoS_x, 2.5	$PhNO_2$	EtOH	70-150	2000	0.5	100	$PhNH_2$	5
" "	$PhCHCH_2$	EtOH	160-190	2300	2.5	0	$PhCH_2CH_3$	5
ReS_2, 0.5	$PhNO_2$	EtOH	110-200	1800	2.0	94	$PhNH_2$	5
ReS_2, 1.0	$PhCHCH_2$	EtOH	150-180	2000	1.0	63	$PhCH_2CH_3$	5
Re_2S_7, 2.5	$PhNO_2$	EtOH	60-100	1900	0.5	100	$PhNH_2$	5
" "	$PhCHCH_2$	EtOH	100-135	1700	1.0	100	$PhCH_2CH_3$	5
Re_2O_7, 2.1 (ex.situ. AcOH)	$PhNO_2$	EtOH	100	2340	12	90	$PhNH_2$	35
" 3.0	$PhCHCH_2$	EtOH	170	3050	2.5	24	$PhCH_2CH_3$	35
" 2.5	Cy=O	EtOH	64	2100	12	86	Cy-OH	35

*The symbol Ph is for the phenyl group, the Cy for the cyclohexyl group, the Ac for the acetyl group, and the Et for the ethyl group.

[33]Adams, Cohen, and Rees, J. Am. Chem. Soc., 49, 1093 (1927).

[34]Kern, Shriner, and Adams, J. Am. Chem. Soc., 47, 1147 (1925).

[35]Shaw, Graham C., "Liquid-Phase Catalytic Hydrogenations with Re_2O_7 Derived Catalysts," a Master's thesis, Brigham Young University, Provo, Utah, 1955.

(d) Temperature. For each hydrogen acceptor there usually exists a well-defined range of temperature with which hydrogen is effectively added. Somewhere in this temperature interval lies the mean effective temperature,[38] i.e., the temperature of maximum saturation velocity. As a rule, hydrogenation is accelerated by a given temperature rise from below the mean effective temperature more than it is retarded by the same temperature increase above this point. Although an increase of temperature affects favorably the speed of a reaction, so that in a given time a greater quantity of product can be obtained, it adversely affects the equilibrium position of a reaction, so that the maximum ultimate yield is decreased. Hence it becomes necessary to work at as low a temperature as possible where the rate of reaction will still be satisfactory. In general, the speed of a reaction may be doubled for every 10 to 15°C increase in temperature. For hydrogenation it usually takes 50°C or more to double the speed.

For the most part, the temperature for hydrogenation is usually below 400°C. In general, the noble metal catalysts, such as platinum or palladium, are used from room temperature to 150°C; catalysts of the nickel and copper type, from 150-250°C; and various combinations of metals and metal oxides, from 250-400°C.[39]

(e) Pressure. Variations of pressure may profoundly

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[38] Ellis, op. cit., p. 29.

[39] Groggins, "Unit Process in Organic Synthesis," 3rd ed., McGraw-Hill Co., New York, 1947, pp. 520-1.

affect the course of hydrogenation. There is sometimes a convenience in working under pressure even for those hydrogenations which will proceed at atmospheric pressure. In liquid phase reactions, increased pressure favors greater solubility of hydrogen, and thus facilitates intimate contact of hydrogen with the hydrogen acceptor and the catalyst. High pressure is to be recommended when it is desired to avoid condensation reactions, these being favored by low concentration of hydrogen on the catalyst surface.[36] Often a high pressure of hydrogen will minimize the poisoning effect of the products as well as their tendency to interact while on the surface of the catalyst, since it will increase the proportion of the surface covered by hydrogen, thus replacing adsorbates. In a similar way, high pressures of hydrogen minimize or eliminate the effect of small amounts of "poisons" present in the reaction mixture.[37]

(f) Time. The time necessary for a hydrogenation reaction may vary from a few seconds to several hours, depending on the substrate, the catalyst, the temperature, the pressure, and the other factors affecting the rate of hydrogenation. In general, the more reactive the compound, the faster the hydrogenation reaction. The time required for a high pressure hydrogenation to attain its equilibrium position is indicated by a cessation of the pressure gauge drop.

(g) Agitation or other means of mixing. In liquid phase reactions, there must be opportunity for intimate contact of hydrogen and hydrogen acceptor with the catalyst. This is usually accomplished by agitation, or rocking the apparatus, or by circulating the hydrogen through the liquid. The rate of hydrogenation is therefore nearly proportional to the speed

at any rate in a wide range, of agitation, rocking or hydrogen circulation.

D. Molybdenum Sulfides as Catalysts in Hydrogenation

Molybdenum sulfides are the most widely used sulfide catalysts; they are relatively unaffected by poisoning, especially by sulfur compounds, but they require high temperatures. Table 2 shows some data of high pressure hydrogenation with molybdenum sulfides as catalysts.

E. Rhenium Heptasulfide as a Catalyst in Hydrogenation

Rhenium heptasulfide is the best sulfide catalyst reported. It is more active than molybdenum sulfides or cobalt polysulfides. It is very stable, extremely resistant to poisoning, and it saturates multiple bond systems without accompanying hydrogenolysis of carbon sulfur bonds. Its disadvantages are its relatively high cost and that it is not as active toward most non-sulfur containing compounds as the "more active" metal catalysts.

Table 3 shows some data[5] of high pressure hydrogenation with rhenium heptasulfide catalyst.

F. Multicomponent Catalysts in Hydrogenation

Alwin Mittasch[2] defined "multicomponent catalysts" as those catalysts which contain mixtures of various chemical constituents rather than one single chemical element or one single chemical compound. To a certain extent, this expression is an arbitrary and vague one. A better definition may be that two or more substances form a multicomponent catalyst

TABLE 2

High Pressure Hydrogenation with Molybdenum Sulfide Catalyst

Catalyst (g/mole of substrate)	Substrate	Solvent	Av.Pres. psi	Av.Temp. °C	Time hrs.	Yields %	Product	Reference
MoS_3	Liquified coal oil (b.p.200-320°C)	—	6250-7350	740	—	60	Light oil (b.p. 200°C)	40
MoS_3	Kogasin oil (synthesized from CO and H_2 under pressure)	—	500	480	—	—	Gasoline	41
MoS_3 on charcoal	PhCOOH	PhH or $PhCH_3$	h.p.	300-360	1.0	94	$PhCH_3$	42
MoS_2	$C_6H_4(CO)_2O$	—	1200	270-280	5.0	70	Ortho-xylene	43
MoS_2 on charcoal	Nitroxylenes	—	600-3000	150-260	—	99	Xylidines	44
MoS_2 on active carbon	$PhNO_2$	—	15	310-320	—	74	$PhNH_2$	45
MoS_2 on Al_2O_3	Thiophene or derivatives	—	2000-5000	230-290	—	—	Thiolane or corresponding derivatives	46
MoS_x	Dicyclohexyl disulfide	dioxane	h.p.	170-185	—	98	Cyclohexane	47
MoS_x	8-Pentadecanone and sulfur	—	2000-3000	120-225	—	78	8-Pentadecane thiol	48
MoS_x	Alkylated heterocyclic compound	—	>300	275-450	—	—	Branched chain saturated hydrocarbons	49
$MoS_{2-3,2.5}$	Styrene	Acetone	2000	120	3.0	8	Ethylbenzene	5

TABLE 2--Continued

Catalyst (g/mole of substrate)	Substrate	Solvent	Av.Pres. psi	Av.Temp. °C	Time hrs.	Yields %	Product	Reference
MoS_{2-3}, 2.5	Cyclohexene	none	2800	250	4.0	22	Cyclohexane	5
" "	Bromobenzene	EtOH	3100	340	4.0	25	Benzene	5
" "	Diphenyl sulfide	EtOH	3600	300	6.5	40	Benzene	5
" "	Benzonitrile	EtOH	2800	325	4.0	85	Toluene (+NH_3)	5
						9	Benzylamine	
" "	Thiophene	none	2400	300	2.5	7	Thiphane+H_2S	5
						33	Thiophene recovery	
" "	Acetophenone	EtOH	2600	200	6.0	18	Methylphenylcarbinol	5
						29	Ethylbenzene	
" "	Cinnamic aldehyde	EtOH	1900	250	5.0	11	Cinnamyl alcohol	5
						23	Hydrocinnamyl alcohol	
						12	Hydrocinnamic aldehyde	
						18	n-Propylbenzene	

[40]Kurokawa and Fujihara, J. Soc. Chem. Ind., Japan, 48, 40-1 (1945) [C. A., 42, 6080 (1948)].

[41]Takenaka, J. Soc. Chem. Ind., Japan, 46, 658-62 (1943) [C. A., 43, 2415 (1949)].

[42]Demann, Krebs and Borchers, Tech. Mitt. Krupp Tech., 6, 59-63 (1938) [C. A., 33, 6257 (1939)].

[43]Yura and Hara, Japan Patent 174,870, June 8, 1948 [C. A., 43, 7507 (1949)].

[44]Gohr, Barr, and Roetheli, U.S. Patent 2,415,817, Feb. 18, 1947 [C. A., 41, 3485 (1947)].

[45]Condit, U.S. Patent 2,560,555, July 17, 1951 [C. A., 46, 3564 (1952)].

[46]Hatch, U.S. Patent 2,648,675, Aug. 11, 1953 [C. A., 48, 8264 (1954)].

[47]Farlow and Signaigo, U.S. Patent 2,402,614, June 25, 1946 [C. A., 40, 5763 (1946)].

[48]Farlow and Signaigo, U.S. Patent 2,402,613, June 25, 1946 [C.A., 40, 5758 (1946)].

[49]Appleby, Lovell, and Love, U.S. Patent 2,429,575, Oct. 21, 1947 [C.A., 42, 1313 (1948)].

TABLE 3

High Pressure Hydrogenation with Rhenium Heptasulfide Catalyst[5]

Substrate	Amt. cat. g/mol of sub.	Solvent	Av.Press. psi	Av.Temp. °C	Time hrs.	% Yield	Product
Styrene	2.5	EtOH	1700	100-135	1.0	100	Ethylbenzene
Phenylacetylene	2.5	EtOH	1900	106-135	1.75	70	Ethylbenzene
Dimethylphenyl-carbinol	2.5	EtOH	2000	130	0.33	100	Cumene
Cyclohexene	0.5	EtOH	2000	240	3.0	92	Cyclohexane
Benzene	2.5	none	3400	300	9.0	57	Cyclohexane
Maleic acid	1.0	water	1300	150	>5	100	Succinic acid
Cinnamic aldehyde	0.5	EtOH	2000	180-200	>7.5	15 29	Hydrocinnamic aldehyde Hydrocinnamyl alcohol
Acetophenone	2.5	EtOH	2300	216-230	0.17	12 85 15	n-Propylbenzene Ethylbenzene Methylphenylcarbinol
Nitrobenzene	2.5	EtOH	1900	60-100	0.5	100	Aniline
p-Nitrobromobenzene	2.5	Methyl-cellosolve	1900	60	0.5	100	p-Bromoaniline
Bromobenzene	2.5	Methyl-cellosolve	3500	320-335	2.5	30 70	Benzene Cyclohexane

TABLE 3--Continued

Substrate	Amt. cat. g/mol of sub.	Solvent	Av.Press. psi	Av.Temp. °C	Time hrs.	% Yield	Product
Benzonitrile	2.5	Ethanol	3000	180-210	0.5	22 58	Benzylamine Dibenzylamine
Allyl phenyl sulfide	2.5	EtOH	1900	150-160	0.5	100	n-Propyl phenyl sulfide
Diphenyl sulfide	2.5	none	2300	280-300	2.0	94	Benzene
Diphenyl disulfide	2.5	Methyl-cellosolve	2200	165-195	1.0	100	Thiophenol
Thiophenol	2.5	Ethanol	3600	300	9.0	60-65 35-40	Benzene Cyclohexane
Thiophene	2.5	none	2000	230-260	3.75	70 0	Thiophane Butyl mercaptan

if their mixtures, made in various proportions, show a promoter action[50] for a certain chemical reaction under constant conditions.

Some of the multicomponent catalysts relating to hydrogenation reported in the literature are cited below.

Ipatiev[51] found that in the presence of copper oxide, and in a copper tube, amylene was only one-third converted into isopentane by hydrogen at 200 atm. at a temperature of 300°C in 28 hours; with copper oxide in an iron tube complete conversion was effected in 12 hours under the same conditions. The same relation holds also for the hydrogenation of cyclohexene, methylcyclohexene, pinene, and carvene.

Ipatiev[52] also found that camphor was hydrogenated in presence of nickel oxide at 320-350°C yielding borneol. This in turn could be dehydrated by alumina at 350-360°C, to yield camphene, which could then be easily hydrogenated at 240°C to give camphane. By using a mixture of nickel oxide and alumina the complete reaction could be effected at a temperature of 200°C or less. Similarly, fenchone may be hydrogenated at 240°C to give fenchyl alcohol, which, however, can only be dehydrated with difficulty. In presence of a mixed nickel oxide-alumina catalyst, a hydrogenation-dehydrogenation process readily occurs at 215°C, yielding fenchane from the original fenchone.

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[50]Refer to p. 3 of this article.

[51]Ipatiev, British Patent 127,609 (1917).

[52]Ipatiev, Ber., 43, 3387 (1910).

The Badische Company[53] stated that hydrogenation of fats with nickel was promoted by the presence of tellurium.

Dewar and Liebmann[53] claimed that a mixture of nickel and copper oxides could be reduced in the oil at 190°C and would hydrogenate cottonseed oil rapidly at that temperature, whereas nickel oxide alone requires a temperature of about 250°C for reduction.

Fokin[54] reported that in catalytic hydrogenations the action of nickel is increased by a second "galvanically acting" metal such as zinc or magnesium.

Prokopers and Filaretov[55] reported that a mixture of molybdenum and cobalt sulfides was more active as a hydrogenation and isomerization catalyst than MoS_2.

Liquid alkene polymers boiling near the gasoline range were reported to be hydrogenated at 175-275°C and 50 atm. by molybdenum or tungsten sulfide mixed with nickel or cobalt sulfide.[56]

Stewart[57] found that MoS_2 associated with 0.5-5% by weight of an alkali oxide, or hydroxide or carbonate, was an

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[53]Ellis, op. cit., p. 52.

[54]Fokin, Elektrochem., 12, 747 (1906) [Frankenburg, Komarewsky, and Rideal, op. cit., p. 83].

[55]Prokopers and Filaretov, J. Applied Chem. (U.S.S.R.), 11, 1631-5, 199-208 (1939) [C.A., 33, 5817 (1939)].

[56]N. V. International Hydrogenation Patents Co., Dutch, 50,935, Sept. 15 (1941) [C.A., 36, 5186 (1942)].

[57]Stewart, U.S. Patent 2,490,488, Dec. 6 (1949) [C.A., 44, 3701 (1950)].

active catalyst for the hydrogenation of oxides of carbon and for the synthesis of normally liquid hydrocarbons and organic oxygenated compounds from CO and hydrogen mixtures by means of Fischer-Tropsch reaction.

A carrier of alumina impregnated with a catalyst comprising sulfides of Mo and of Fe, or Co, or Ni was reported to be used for the hydrogenation of butene dimers at 25°C and 150 atm.[58]

G. Analyses of Rhenium, Molybdenum, and Sulfur

1. Analysis of Rhenium.[59] Determination of rhenium can be made by gravimetric, volumetric, colorimetric, and electrometric methods. However, none of the methods are entirely satisfactory, even when used in determination of rhenium in pure compounds as $KReO_4$. Probably only the tetraphenylarsonium-perrhenate method is worth considering for the determination of rhenium in a solution containing both rhenium and molybdenum compounds.

There are three gravimetric methods generally used for the determination of rhenium:

(a) Metallic rhenium method. Rhenium is converted to Re_2S_7 and ignited to metal at about 900°C under hydrogen. Molybdenum is an interfering element.

(b) Nitronperrhenate method. Rhenium is precipitated

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[58]N. V. de Bataafsche Petroleum Maatschappy, Dutch Patent, 67,093, Jan. 15 (1951) /C.A., 45, 5919 (1951)/.

[59]Hillebrand, Lundell, Bright, Hoffman, "Applied Inorganic Analysis," 2nd ed., John Wiley & Sons, New York, 1953, pp. 317-26.

by nitron and weighed as nitronperrhenate. Molybdenum is also an interfering element.

(c) Tetraphenylarsoniumperrhenate method. Rhenium is precipitated by tetraphenylarsonium chloride in solutions varying from strongly ammonical (6M) to moderately acidic (5M HCl) and weighed as $(C_6H_5)_4AsReO_4$. Molybdenum does not interfere if precipitation is made in solutions containing ammonium hydroxide (6M) or tartaric acid (0.6M).

Two volumetric methods are capable of yielding good results under ideal conditions:

(a) Perrhenic acid method. Rhenium is determined by converting it to perrhenic acid and then titrating with standard alkali. The chief difficulty lies in converting rhenium to the acid without introducing other acids.

(b) Permanganate method. This method is based on the reduction of rhenium in a Jones reductor provided with a solution of ferric sulfate in the receiver followed by titration with a standard solution of permanganate. Only small amounts less than 30 mg. of Re can be handled; besides molybdenum, which undergoes reduction and oxidation under similar circumstances, must be separated first.

The colorimetric method, which is usually confined to amounts of rhenium ranging from 0.0005 to 0.5 mg., is based on the brownish yellow compound of rhenium, said to be $ReO(CNS)_4$, which is formed when a hydrochloric acid solution of a perrhenate is treated with a mixture of $SnCl_2$ and KCNS. However, molybdenum is also the chief interfering element.

Electrolytic methods that have been developed for the determination of rhenium are not very satisfactory.

2. Analysis of Molybdenum[60]

The volumetric method is based on the reduction of molybdenum in a Jones reductor. The solution is caught under a solution of ferric sulfate and titrated with a standard solution of potassium permanganate. This method is an accurate and convenient one for the determination of molybdenum from a pure molybdenum compound. However, in presence of rhenium, this method cannot be used for the determination of either rhenium or molybdenum, as already mentioned in the volumetric determination of rhenium, unless they are separated first.

Three gravimetric methods are recommended, of which the α-benzoinoxime and lead molybdate methods are probably used for the determination of molybdenum in a solution containing both molybdenum and rhenium compounds.

(a) α-Benzoinoxime method. Molybdenum is precipitated by α-benzoinoxime, ignited at 500-525°C, weighed as MoO_3. Rhenium is not precipitated when it occurs alone, and probably not when associated with molybdenum.

(b) Lead molybdate method. Molybdenum is precipitated by lead acetate as $PbMoO_4$, ignited and weighed as $PbMoO_4$.

(c) Sulfide method. The determination of molybdenum by precipitation as sulfide, followed by ignition to the oxide MoO_3, is not quite as satisfactory a method as the foregoing

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[60]Hillebrand, Lundell, Bright, Hoffman, op. cit., pp. 302-16.

ones. It is difficult to completely precipitate MoS_3 and to satisfactorily ignite MoS_3 to MoO_3; besides, rhenium is an interfering element.

In the event one has a milligram or less of molybdenum, it is better to determine the element colorimetrically by the use of the stannous chloride thiocyanate reaction, preferably after first separating it as the sulfide. However, rhenium interferes in the usual thiocyanate colorimetric method for molybdenum.

3. Analysis of Sulfur[61]

The oxidation of sulfur to sulfate ion, followed by precipitating it as barium sulfate by barium chloride, is the generally used method for the determination of sulfur. The accuracy of this method is dependent on the working conditions.

The determination of the sulfate ion by precipitation with barium chloride in a solution containing only sulfuric acid is subject to a negative error caused by the solubility of the precipitated barium sulfate in the solution and in the wash water and to a positive error caused by the coprecipitation of barium chloride.

When the sulfate ion is precipitated in a solution containing sulfates of the alkalies, two other sources of error, both negative, are introduced, one caused by the coprecipitation of alkali sulfate, the other by the coprecipitation of acid alkali sulfate.

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[61] Ibid., pp. 711-23.

Three volumetric methods for the determination of sulfur are recommended:

(a) The benzidine method for large amounts of sulfur as in pyrite.

(b) The barium chromate method for moderate amounts of sulfur as in coal.

(c) The evolution method for small amounts of sulfur as in steel.

All are reported to be well suited for routine analyses.

Small amounts of soluble sulfates are best determined in a nephelometer. Very small amounts of sulfur (such as 0.001 mg.), occurring as easily decomposed sulfide, are conveniently determined colorimetrically by comparing stains produced on lead acetate paper with those produced by a standard.

A photometric method for the determination of sulfur in metals is described by C. L. Luke.[62]

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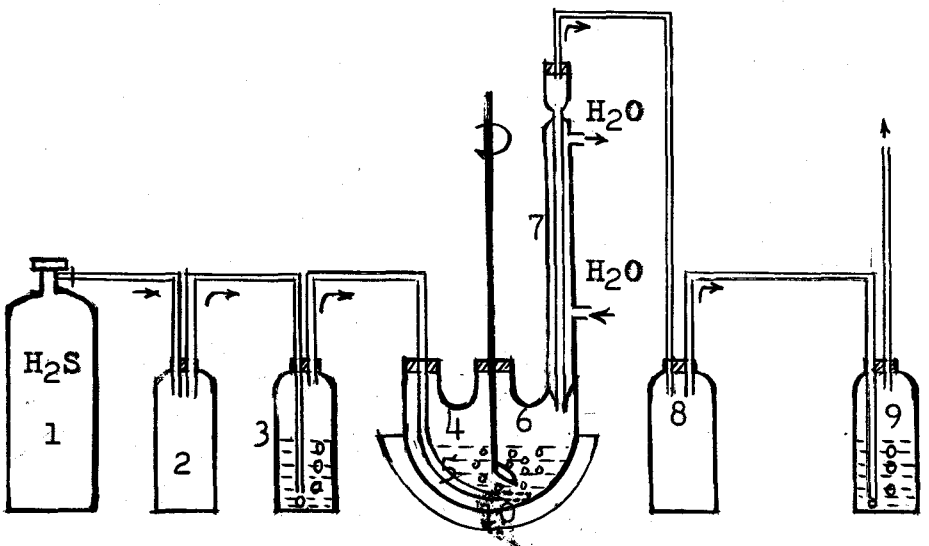
[62]Luke, Anal. Chem., 11, 1369 (1949).

III. EXPERIMENTAL

A. The Preparation of Catalysts.

1. The Precipitation of Mixtures of Rhenium and Molybdenum Sulfides by Saturating Acid Solutions of Perrhenate and Molybdate with Hydrogen Sulfide.

(a) General procedure. A gas absorption apparatus was arranged as shown in Fig. 4 under hood.



1 = Hydrogen sulfide gas cylinder
2 and 8 = Safety bottles
3 and 9 = Bubble counting bottles
4 = Reactor
5 = Gas dispersion tube
6 = Stirrer
7 = Water cooled condenser
10 = Heating mantle

Fig. 4.--An Arrangement of Hydrogen Sulfide Gas Absorption Apparatus.

Calculated amounts of potassium or ammonium perrhenate ($KReO_4$ or NH_4ReO_4) and ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$) were weighed such that they would form, if

being completely precipitated by H_2S, a mixture of rhenium heptasulfide and molybdenum trisulfide in suitable proportion, i.e., 100:0,80:20,50:50,20:80, 0:100. They were added, together with an appropriate volume of dilute hydrochloric acid of certain concentration (0.25N,0.3N,1N,2.5N,3N and 5N), to the three-necked round bottom flask.

The solution was heated to boiling. A rapid stream of hydrogen sulfide was passed into the solution until it was saturated, or the reaction was in equilibrium, which was indicated by the bubbling speed of the gas passing through the measuring bottles before and after the reactor. It took less than 20 minutes. However, an hour or more was usually taken to make sure that the precipitation would be nearly complete.

The colorless solution turned to blue at first, due to the formation of molybdenum blue, $Mo_3O_8.xH_2O$, or more exactly $Mo_8O_{23}.xH_2O$, and then quickly turned to brown and finally to dark brown or black when rhenium and molybdenum sulfides were precipitated. Then the gas was turned off, the apparatus cooled and allowed to stand overnight.

The dark brown suspension was filtered easily through a fine sintered glass crucible. The precipitate was washed with H_2S-saturated water and then a small amount of distilled water. The filtrate was usually of brown color, which indicated that the precipitation of molybdenum was not complete. A considerable amount of a second precipitate containing a high percentage of molybdenum could be obtained if the filtrate of the first precipitate was diluted with water and treated

again with hydrogen sulfide.

The precipitate was dried in a desiccator over anhydrous $CaCl_2$ under a reduced pressure of about 20 mm. for several days until it was dry enough to be pulverized in a mortar with a pestle. The fairly dry, powdered precipitate was then transferred into a weighed vial and heated to a constant weight in a vacuum pistol over P_2O_5 under a high vacuum, usually 50-100 microns, with bromobenzene as heating medium.

(b) Chemical reactions

$$(NH_4)_6Mo_7O_{24}\cdot + 24\ H_2S \rightarrow 7\ MoS_3\downarrow + 3\ (NH_4)_2S + 24\ H_2O$$

$$3\ (NH_4)_2S + 6\ HCl \rightarrow 3\ H_2S\uparrow + 6\ NH_4Cl$$

$$(NH_4)_6Mo_7O_{24} + 21\ H_2S + 6\ HCl \rightarrow 7MoS_3\downarrow + NH_4Cl + 24\ H_2O$$

$$2ReO_4^- + 8\ H_2S \rightarrow Re_2S_7\downarrow + S^= + 8\ H_2O$$

$$S^= + 2\ HCl \rightarrow 2\ Cl^- + H_2S\uparrow$$

$$2\ ReO_4^- + 7\ H_2S + 2\ HCl \rightarrow Re_2S_7\downarrow + 2\ Cl^- + 8\ H_2O$$

(c) Experimental data. The experimental data are summarized in Table 4.

2. The Precipitation of Mixtures of Rhenium and Molybdenum Sulfides by Saturating Alkaline Solutions of Perrhenate and Molybdate with Hydrogen Sulfide followed by Acidification with Dilute Sulfuric or Hydrochloric Acid.

(a) General procedure. The general procedure was the

TABLE 4

Conditions of Catalyst Preparation

Code Symbols: R for Re_2S_7, M for MoS_3, Ah for hydrochloric acid, As for sulfuric acid, Ba for ammonium hydroxide, T for sodium thiosulfate, W for water, N for normality.

Type	Code Number	Substrate	Solution	% of Substrate in Solution	Reagent	% Yield (dry basis)	Color	Remarks
MoS_3	RO-M100-Ah-N5-1	$(NH_4)_6Mo_7O_{24}.4H_2O$	5N HCl	13	H_2S	25.8	brown	H_2S, 15 min.
MoS_3	RO-M100-Ah-N5-2	"	5N HCl	10	H_2S	20.0	brown	H_2S, 30 min.
MoS_3	RO-M100-Ah-N3-1	"	3N HCl	13	H_2S	40.3	brown	H_2S, 1 hr.
MoS_3	RO-M100-Ah-N3-2	"	3N HCl	13	H_2S	24.2	brown	H_2S, 1 hr., ppt washed with large amt. of water.
MoS_3	RO-M100-Ah-N2.5-4	"	2.5N HCl	5	H_2S	54.2	dark br.	H_2S, 1 hr., diluted the filtrate to 1N, H_2S, 1 hr. again
MoS_3	RO-M100-Ah-N1-2	"	1N HCl	10	H_2S	53.7	brown	H_2S, 30 min.
MoS_3	RO-M100-Ah-N0.3-1	"	0.3N HCl	13	H_2S	36.0*	dark br.	H_2S, 1 hr.
MoS_3	RO-M100-Ah-N0.3-2	"	0.3N HCl	10	H_2S	68.2	dark br.	H_2S, 1 hr.
MoS_3	RO-M100-Ah-N0.25-1	"	0.25N HCl	10	H_2S	85.1	brown	H_2S, 30 min.
MoS_3	RO-M100-As-N0.5-1	"	1.35-0.5N H_2SO_4	10	H_2S	69.5	dark br.	H_2S, 30 min.+ 30 min.
MoS_3	RO-M100-W-N0-1	"	H_2O	10	H_2S	92.3	black	H_2S, 30 min., acidified with HCl.

TABLE 4--Continued

Type	Code Number	Substrate	Solution	% of Substrate in Solution	Reagent	% Yield (dry basis)	Color	Remarks
MoS_3	RO-M100-Ba-NO.25-1	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	0.25N NH_4OH	10	H_2S	77.1	dark br.	H_2S, 30 min. at room temp., acidified with HCl.
MoS_3	RO-M100-Ba-NO.25-2	"	0.25N NH_4OH	10	H_2S	89.7	dark br.	H_2S, 30 min., acidified with HCl
MoS_3	RO-M100-Ba-N2.5-1	"	2.5N NH_4OH	10	H_2S	100	brown	H_2S, 30 min., acidified with HCl
MoS_3	RO-M100-Ba-N2.5-4	"	2.5N NH_4OH	5	H_2S	98.6	brown	H_2S, 1 hr., acidified with HCl
MoS_3	RO-M100-Ba-N5-1	"	5N NH_4OH	10	H_2S	100	brown	H_2S, 30 min., acidified with HCl
MoS_3	RO-M100-T-As-2	"	0.5N H_2SO_4	3	$Na_2S_2O_3$	40.3	dark br.	Boiled 30 min., neutralized with NH_4OH, extracted with toluene for 7 days.
MoS_3	RO-M100-T-As-3	"	1.6N H_2SO_4	5	$Na_2S_2O_3$	53	brown	Boiled 2 hrs., neutralized with NH_4OH, extracted with toluene for 24 hrs.
Re_2S_7	R100-MO-Ah-N6-1	$KReO_4$	6N HCl	2.5	H_2S	77.5*	black	H_2S, 1 hr.
Re_2S_7	R100-MO-Ah-N5-1	$KReO_4$	5N HCl	3	H_2S	81.5*	black	H_2S, 3 hrs.
Re_2S_7	R100-MO-Ah-NO.251	$KReO_4$ + NH_4ReO_4	0.25N HCl	5	H_2S	92.0	black	H_2S, 1 hr.

TABLE 4--Continued

Type	Code Number	Substrate	Solution	% Substrate in Solution	Reagent	% Yield (dry basis)	Color	Remarks
Re_2S_7	R100-M0-Ba-N0.25-1	NH_4ReO_4	0.25N NH_4OH	5	H_2S	99.9	black	H_2S,40 min.,acidified with HCl; diluted the filtrate to 4N HCl, H_2S, 30 min.
Re_2S_7	R100-M0-Ba-N5-1	$KReO_4$	5N NH_4OH	2	H_2S	66.0	black	H_2S, 30 min. at 70°C.
Re_2S_7	R100-M0-T-As-3	$KReO_4$	1N H_2SO_4	3	$Na_2S_2O_3$	70.5	black	Boiled 1.5 hrs., extracted with toluene for 24 hrs.
Re_2S_7	R100-M0-T-As-4	$KReO_4$	0.85N H_2SO_4	5	$Na_2S_2O_3$	64.7	black	Boiled 70 min., extracted with toluene for 24 hrs.
$Re_2S_7.MoS_3$	R80-M20-Ah-N5-2	$KReO_4$ + $(NH_4)_6Mo_7O_{24}.4H_2O$	5N HCl	5	H_2S	82.5	black	H_2S, 1.5 hrs.
$Re_2S_7.MoS_3$	R80-M20-Ah-N2.5-4	NH_4ReO_4 + $(NH_4)_6Mo_7O_{24}.4H_2O$	2.5N HCl	5	H_2S	86.0	black	H_2S, 1 hr.
$Re_2S_7.MoS_3$	R80-M20-Ah-N0.25-3	$KReO_4$ + $(NH_4)_6Mo_7O_{24}.4H_2O$	0.25N HCl	5	H_2S	88.0	black	H_2S, 1 hr.;contaminated by sublimed P_2O_5.

TABLE 4--Continued

Type	Code Number	Substrate	Solution,	% of Substrate in Solution	Reagent	% Yield (dry basis)	Color	Remarks
$Re_2S_7.MoS_3$	R80-M20-Ba-N0.25-3	$KReO_4$ + $(NH_4)_6Mo_7O_{24}.4H_2O$	0.25N NH_4OH	5	H_2S	86.5	black	H_2S, 30 Min., acidified with H_2SO_4; contaminated by sublimed P_2O_5.
$Re_2S_7.MoS_3$	R80-M20-Ba-N2.5-4	NH_4ReO_4 + $(NH_4)_6Mo_7O_{24}.4H_2O$	2.5N NH_4OH	5	H_2S	99.0	black	H_2S, 30 min., acidified with H_2SO_4.
$Re_2S_7.MoS_3$	R80-M20-Ba-N5-1	$KReO_4$ + $(NH_4)_6Mo_7O_{24}.4H_2O$	5N NH_4OH	3	H_2S	90.0	black	H_2S, 30 min., acidified with H_2SO_4; further H_2S, 10 min.
$Re_2S_7.MoS_3$	R80-M20-T-As-1	"	2.5N H_2SO_4	5	$Na_2S_2O_3$	61.5	black	Boiled 45 min., extracted with toluene for 21 days.
$Re_2S_7.MoS_3$	R80-M20-T-As-3	"	1.6N H_2SO_4	5	$Na_2S_2O_3$	77.1	black	Boiled 70 min., extracted with toluene for 24 hrs.
$Re_2S_7.MoS_3$	R68-M32-Ah-N6-1	"	6N HCl	5	H_2S	64.1*	dark br.	H_2S, 75 min.
$Re_2S_7.MoS_3$	R50-M50-Ah-N5-2	"	5N HCl	5	H_2S	79	dark br.	H_2S, 1.5 hrs.; loss of vacuum on heating at 258°C because of leakage.
$Re_2S_7.MoS_3$	R50-M50-Ah-N2.5-4	NH_4ReO_4 + $(NH_4)_6Mo_7O_{24}.4H_2O$	2.5N HCl	5	H_2S	89.5	black	H_2S, 1 hr.

TABLE 4--Continued

Type	Code Number	Substrate	Solution	% of Substrate in Solution	Reagent	% Yield (dry basis)	Color	Remarks
$Re_2S_7.MoS_3$	R50-M50-Ba-N2.5-4	NH_4ReO_4 + $(NH_4)_6Mo_7O_{24}.4H_2O$	2.5N NH_4OH	5	H_2S	97.0	brownish black	H_2S, 1 hr., acidified with H_2SO_4.
$Re_2S_7.MoS_3$	R50-M50-Ba-N5-1	$KReO_4$ + $(NH_4)_6Mo_7O_{24}.4H_2O$	5N NH_4OH	3	H_2S	92.5	"	H_2S, 30 min., acidified with H_2SO_4; further H_2S, 10 min.
$Re_2S_7.MoS_3$	R50-M50-T-As-1	"	2N H_2SO_4	5	$Na_2S_2O_3$	27.1	black	Boiled 45 min., extracted with toluene for 21 days.
$Re_2S_7.MoS_3$	R50-M50-T-As-3	"	1.6N H_2SO_4	5	$Na_2S_2O_3$	72.8	black	Boiled 70 min., extracted with toluene for 24 hrs.
$Re_2S_7.MoS_3$	R40-M60-Ah-N6-1	"	6N HCl	5	H_2S	59.6*	brown	H_2S, 75 min.
$Re_2S_7.MoS_3$	R20-M80-Ah-N5-2	"	5N HCl	5	H_2S	50.6	brown	H_2S, 1.5 hr., loss of vacuum on heating at 258°C.
$Re_2S_7.MoS_3$	R20-M80-Ah-N2.5-4	NH_4ReO_4 + $(NH_4)_6Mo_7O_{24}.4H_2O$	2.5N HCl	5	H_2S	68.4	black	H_2S, 1 hr.
$Re_2S_7.MoS_3$	R20-M80-Ba-N2.5-4	"	2.5N NH_4OH	5	H_2S	100	brown	H_2S, 1 hr., acidified with H_2SO_4.

TABLE 4--Continued

Type	Code Number	Substrate	Solution	% of Substrate in Solution	Reagent	% Yield (dry basis)	Color	Remarks
$Re_2S_7.MoS_3$	R20-M80-Ba-N5-1	$KReO_4$ + $(NH_4)_6Mo_7O_{24}.4H_2O$	5N NH_4OH	3	H_2S	90.0	dark br.	H_2S, 30 Min., acidified with H_2SO_4.
$Re_2S_7.MoS_3$	R20-M80-T-As-1	"	1.5N H_2SO_4	5	$Na_2S_2O_3$	37.7	black	Boiled 45 min., extracted with toluene for 7 days.
$Re_2S_7.MoS_3$	R20-M80-T-As-2	"	2N H_2SO_4	5	$Na_2S_2O_3$	25.2	black	" but loss of vacuum on heating at 258°C.
$Re_2S_7.MoS_3$	R20-M80-T-As-3	"	1.6N H_2SO_4	5	$Na_2S_2O_3$	65.0	black	Boiled 70 min., extracted with toluene for 24 hrs.
$Re_2S_7.MoS_3$	R18-M82-Ah-N6-1	"	6N HCl	5	H_2S	67.0	brown	H_2S, 75 min.

*Some of the catalyst was lost when the vacuum pump was operated due to the presence of excessive moisture in the catalyst.

same as that of the precipitation from acid solutions except that ammonium hydroxide was used instead of hydrochloric acid.

When the boiling alkaline solution was treated with hydrogen sulfide, it gradually turned to yellow, orange, dark red, and finally to reddish black as it became neutral to litmus paper. However, the precipitation was far from complete until the solution was cooled down, acidified with dilute sulfuric acid, and allowed to stand overnight.

The precipitate was somewhat colloidal and voluminous. A very small amount of a second precipitate could be obtained if the colorless filtrate was treated again with hydrogen sulfide.

(b) Chemical reactions

$$(NH_4)_6Mo_7O_{24} + 24\ H_2S \rightarrow 7\ MoS_3\downarrow + 3(NH_4)_2S + 28\ H_2O$$

$$NH_4OH + H_2S \rightarrow (NH_4)_2S + 2\ H_2O$$

$$MoS_3 + (NH_4)_2S \rightarrow (NH_4)_2MoS_4$$

$$(NH_4)_2MoS_4 + H_2SO_4 \rightarrow MoS_3\downarrow + (NH_4)_2SO_4 + H_2S\uparrow$$

$$2\ ReO_4^- + 8\ H_2S \rightarrow Re_2S_7\downarrow + S^= + 8\ H_2O$$

$$Re_2S_7 + (NH_4)_2S \rightarrow 2\ NH_4ReS_4$$

$$2\ NH_4ReS_4 + H_2SO_4 \rightarrow Re_2S_7\downarrow + (NH_4)_2SO_4 + H_2S\uparrow$$

(c) Experimental data. The experimental data are summarized in Table 4.

3. The Precipitation of Mixtures of Rhenium and Molybdenum Sulfides by Treating Thiosulfate Solutions with Dilute Sulfuric Acid Solutions of Perrhenate and Molybdate.

(a) General procedure. A 3-5% solution of calculated

amounts of potassium perrhenate and ammonium molybdate tetrahydrate dissolved in sulfuric acid (0.5-2.5) was added to a three-necked round bottom flask equipped with a stirrer, a water condenser, and a graduated funnel. The solution was heated to boiling. A 20-40% sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) solution was added, in 200-250% excess, drop by drop from the funnel, with good stirring. The solution was kept boiling and stirring for a further half hour. The colorless solution turned to blue, brown, and finally greyish brown or brownish black when mixture of the sulfides was precipitated.

The solution was cooled and filtered through a fine sintered glass crucible. The filtrate was usually dark blue or brown in color, depending upon the relative amounts of molybdenum and rhenium remaining in it. The precipitate was washed with distilled water. It was dried in a desiccator over anhydrous $CaCl_2$ under a reduced pressure of about 20 mm. for several days. The fairly dry, pulverized precipitate was then transferred to an extraction thimble and treated with toluene for 24 hours. Molybdenum sulfide, even rhenium sulfide as well as free sulfur, could be extracted by toluene by prolonged extraction. After extraction, the precipitate was transferred to a vial and dried in a vacuum pistol as mentioned in section 1-(a), page 34.

(b) Chemical reactions

$$(NH_4)_6Mo_7O_{24} + 21\ Na_2S_2O_3 + 3\ H_2SO_4 \rightarrow 7\ MoS_3\downarrow + 21\ Na_2SO_4 + 3(NH_4)_2SO_4 + 3\ H_2O$$

$$2\ KReO_4 + 7\ Na_2S_2O_3 + H_2SO_4 \rightarrow Re_2S_7\downarrow + 7\ Na_2SO_4 + K_2SO_4 + H_2O$$

(c) Experimental data. The experimental data are summarized in Table 4.

B. The Analyses of Catalysts

1. Control Tests for the Preparation of Solutions from Mixtures of Rhenium and Molybdenum Sulfides by Different Oxidizing Reagents.

Molybdenum sulfide can be oxidized readily to molybdic and sulfuric acids, and rhenium sulfide less readily to perrhenic and sulfuric acids, by such oxidizing agents as strong nitric acid, aqua regia, bromine water, hydrogen peroxide in alkaline solution and sodium peroxide (fusion) or sodium carbonate and nitrate (fusion).[63] The object of the tests was to select a suitable oxidizing reagent which would bring molybdenum and rhenium sulfides effectively into solution, but would not interfere with the reagents used for the subsequent analyses of rhenium, molybdenum and sulfur, and also would be convenient to work with.

The following four common oxidizing reagents with accompanying working procedures were recommended in the literature for attacking molybdenum or rhenium sulfide. In the tests, catalyst of code number R50-M50-T-As-3[64] was used as the sample.

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[63]Hillebrand, Lundell, Bright, and Hoffman, op. cit., pp. 303, 318.

[64]Refer to Table 4, p. 39 of this article.

(a) Mixture of concentrated sulfuric and nitric acids.[65] Ca. 0.5 g. of a dry, pulverized sample of mixture of rhenium and molybdenum sulfides was weighed accurately to the tenth milligram into a 250 ml. beaker. It was then treated with about 10 ml. of concentrated nitric acid. Brown fumes were evolved. The solution was heated gently until no dark residue remained, and the decomposition was complete. Three 10 ml. portions of concentrated nitric acid were required to effect the decomposition. Only light pink residue was observed. About 10 ml. of concentrated sulfuric acid was then added and the solution was heated to strong fumes of SO_3. All the residue went into solution, which was then dark brown in color, probably due to the existence of organic matter.

The solution was cooled and treated with 5 ml. of concentrated nitric acid and again heated to strong white fumes. It turned colorless. The solution was cooled again and the cover and sides of the beaker were washed down very carefully with a little water and again heated to strong white fumes of SO_3 to make sure of the expulsion of nitric acid. About 5 ml. of sulfuric acid was left. The solution was cooled and about 50 ml. of distilled water was added and digested until all soluble salts were in solution.

The cooled colorless solution was then diluted to 100 ml. in a volumetric flask for the determination of rhenium and

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[65] Hillebrand, Lundell, Bright, and Hoffman, op. cit., p. 309; also Kennecott Copper Corp., Utah Copper Division, "Assay Method for High Grade Molybdenite, Control Samples," unpublished paper.

molybdenum. Sulfur was not determined by this method since sulfuric acid was used as a reagent.

(b) Sodium peroxide (Parr Bomb Method[66])

Ca. 0.25 g. each of two dry, pulverized samples were weighed by difference into two fusion cups. About 0.75 g. of potassium perchlorate as an accelerator and 0.9 g. of pure sucrose were added to each sample. They were then mixed by stirring with a clean glass rod. One measure full of sodium peroxide (app. 15 g.) was quickly removed from the tightly closed jar and placed in each bomb with the sample and accelerator. The bomb was tightly closed with a wrench. The contents were thoroughly mixed by shaking and rotating. The bomb was then placed inside the ignition housing with about 2 ml. of water in the lid depression to serve as an ignition indicator. It was ignited at the bottom with a hot flame of a Meker burner. Within five minutes or less, the water on the cover started to boil due to an advanced thermal reaction within the bomb. The bomb was immediately grasped with tongs and quenched in a large amount of cold water until it was thoroughly cooled. The bomb was opened and examined. If the ignition was successful the contents would appear molten or sintered. Any material adhering to the lid was washed into a 600 ml. beaker with the bomb cups which were just covered with about 200 ml. of water. The beaker, protected with a watch glass, was set on a steam plate. When the fused mass was

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[66]Dr. H. Smith Broadbent, "The Determination of Sulfur in Organic Compounds by the Parr Bomb Method," unpublished paper, Brigham Young University, Provo, Utah.

dissolved, the cups were removed from the beaker with a glass rod and rinsed off well with water. The dark brown suspension was filtered through a weighed sintered glass crucible. The black residue in the crucible was dried to constant weight at 110°C. The dark brown filtrate was diluted to 500 ml. in a volumetric flask for the determination of molybdenum and sulfur contents. Since the solution contained perchlorate ion, which would interfere with the precipitation of rhenium by tetraphenyl arsonium chloride,[67] the rhenium content was not determined.

(c) Aqua regia and bromine[68]

Ca. 0.5 g. of a dry, pulverized sample was weighed accurately to the tenth milligram into a 250 ml. beaker. It was treated with 12 ml. of a mixture of three parts of nitric acid (9 ml.) and one part of hydrochloric acid (3 ml.) to which 4 or 5 drops of bromine had been added. The beaker was covered with a watch glass. The mixture was cooled with ice water to prevent the reaction from becoming too violent. Then the reaction was allowed to proceed at room temperature for half an hour with occasional shaking of the beaker. A brown solution with some black residue was observed. It was heated gently until all apparent action had subsided. The residue went into solution and brown fumes effervesced. The cover was raised and the liquid was evaporated to dryness. Some blue residue

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[67]Hillebrand, Lundell, Bright, and Hoffman, op. cit., p. 321.

[68]Ibid., p. 713.

was left. Ca. 5 ml. of hydrochloric acid was added. The cover was replaced and the hydrochloric acid solution was heated until effervescence ceased. The solution was still of brown color. The cover and the sides of the beaker were washed with water. The solution was evaporated again to dryness. The blue residue was treated with 25 ml. of hot water and stirred until it was disintegrated. The residue, if any, was filtered into a weighed sintered glass crucible and the blue filtrate was diluted to 100 ml. in a volumetric flask for the determination of rhenium, molybdenum, and sulfur.

(d) Hydrogen peroxide in alkaline solution

Ca. 0.5 g. of a dry, pulverized sample was weighed accurately into a 100 ml. beaker. About 10 ml. of 5 N ammonium hydroxide solution was added. The beaker was then covered with a watch glass. Thirty per cent hydrogen peroxide in 0.5 ml. portions was added with shaking of the beaker or stirring with a glass rod and occasional cooling in water. A total amount of 10 ml. of 30% hydrogen peroxide was used, which is about four times the theoretical amount required for the sample. However, the solution was still of light yellow color and some light brown residue was observed. The solution was then heated to near boiling in order to destroy the excess hydrogen peroxide. The light brown residue was filtered into a weighed sintered glass crucible. The light yellow filtrate was diluted to 100 ml. with distilled water in a volumetric flask for the determination of rhenium, molybdenum, and sulfur.

For the subsequent analyses, molybdenum was determined by the "α-benzoinoxime" method;[69] rhenium by the "tetraphenylarsonium perrhenate" method[70] from a 6 M ammonium hydroxide solution; and sulfur by the "barium sulfate" method.[71] The data are summarized in Table 5.

2. Blank Tests of Various Methods for the Determination of Rhenium and Molybdenum

The objects of these tests were to select relatively accurate and convenient methods for the determination of rhenium or molybdenum in a solution containing pure rhenium compound, pure molybdenum compound, and especially a mixture of them. For convenience, blank test solutions containing certain definite amounts of rhenium and molybdenum were prepared from calculated amounts of $KReO_4$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ as follows:

Solution No. 1. A 50 ml. of the solution contains 0.081514 g. of Re and Mo, (Re:Mo = 1:1).

Solution No. 2. A 50 ml. of the solution contains 0.16303 g. of Mo and 0.018114 g. of Re, (Re:Mo = 1:9).

Solution No. 3. A 50 ml. of the solution contains 0.081514 g. of Mo and 0.32606 g. of Re (Re:Mo = 4:1).

(a) Blank test of the "tetraphenylarsonium perrhenate"

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[69]Refer to (g), p. 60 of this article.

[70]Refer to (b), p. 51 of this article.

[71]Refer to p. 67 of this article.

TABLE 5

Control Test for the Determination of Rhenium, Molybdenum, and Sulfur from the Same Sample of Code Number R50-M50-T-As-3[64] Using Different Oxydizing Reagents for the Preparation of Solution

Ex. No.	Weight of Sample, g.	Reagent	Weight of Residue, g. (% of sample)	Weight of Precipitate, g. R for Ph_4AsReO_4 B for $BaSO_4$ M for MoO_3	% Wet Basis (% Dry Basis) Re for Rhenium S for Sulfur Mo for Molybdenum H_2O# for the remainder
1	0.5002	Conc.H_2SO_4 and Conc.HNO_3	0	R 0.0162 B M 0.0740	Re 4.76 S not determined Mo 19.72*
2	0.5079	Na_2O_2, $KClO_4$, and sucrose	0.0456 (9.0%)	R B 0.0608 M 0.0284	Re not determined S 9.03 Mo 8.19
3	0.5082	Aqua regia and bromine	0.0169 (3.3%)	R 0.0676 B 0.1259 M 0.0684	Re 20.23 S 35.20* Mo 18.56*
4	0.5015	30% H_2O_2 in dil. NH_4OH	0.0022 (0.44%)	R 0.1020 B 0.1247 M 0.0742	Re 30.05* (35.70) S 34.32* (40.70) Mo 19.82* (23.60) H_2O# 15.81

*Those data seem to be nearly correct.

#Inasmuch as the percentages of rhenium, molybdenum, and sulfur did not total 100%, it was supposed that the remainder was moisture.

method[72] for the determination of rhenium in a solution containing a known amount of rhenium alone.

A sample of c.p. potassium perrhenate containing about 40 mg. of rhenium was weighed into a 125 ml. conical flask. An aliquot amount of distilled water was added in order to make the final solution about 50 ml. in volume. It was then added to 20 ml. of concentrated ammonium hydroxide solution to make the final solution of 6 M., or 21 ml. of concentrated hydrochloric acid to make the final solution of 5 M. Then 1.46 g. of sodium chloride was also added to make the final solution containing about 0.5 M. of NaCl.

The solution was heated to near boiling and an excess of 1% tetraphenylarsonium chloride solution was added to it with good stirring. The flask was stoppered if the precipitation was made in 6 M ammonium hydroxide solution. It was allowed to stand at room temperature overnight. The white precipitate was filtered through a weighed Gooch crucible and the filtrate was tested with 1% tetraphenylarsonium chloride solution for complete precipitation. The precipitate was then washed several times with ice water and dried to constant weight in an electric oven at 110°C. It was weighed as Ph_4AsReO_4.

The data are tabulated in Table 6.

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[72]Hillebrand, Lundell, Bright, and Hoffman, op. cit., p. 321.

TABLE 6

Blank Test for the Determination of Rhenium by Tetraphenylarsonium Perrhenate Method from Either 6M Ammonium Hydroxide or 5M Hydrochloric Acid Solution Containing Rhenium Compound Alone

Sample No.	1	2
Weight of $KReO_4$, g.	0.06213	0.06213
Equivalent weight of rhenium, g.	0.0400	0.0400
Water, ml.	18	17
Conc. NH_4OH, ml.	20	0
Conc. HCl, ml.	0	21
NaCl, g.	1.46	1.46
Volume of 1% Ph_4AsCl solution, ml.	12	12
Wt. of Ph_4AsReO_4, g.	0.1369	0.1320
Wt. of Re found, g.	0.04025	0.03881
% of error, %	+0.625	-2.98

(b) Blank test of the "tetraphenylarsonium perrhenate" method[72] for the determination of rhenium in a solution containing known amounts of rhenium and molybdenum.

An aliquot portion of the prepared blank test solution was pipetted, or appropriate amounts of c.p. potassium perrhenate and ammonium molybdate tetrahydrate were weighed into a 125 ml. conical flask. A calculated amount of water was added such that the final solution would be ca. 50 ml. in volume. A 20 ml. of concentrated ammonium hydroxide was added

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in order to make the final solution of 6M, or 5.05 g. of tartaric acid monohydrate (M.W. 168.1), to make the final solution of 0.6M. Also, instead of adding ammonium hydroxide or tartaric acid, a sample was chosen to be treated with 21 ml. of concentrated hydrochloric acid to make the final solution of 5M in order to compare with the interference of molybdenum present.

The rest of the procedure was exactly the same as that mentioned in the preceding section (a). The filtrates combined with their washings were saved for further determination of molybdenum by the permanganate titration method in section (f), page 58.

The data are tabulated in Table 7.

(c) Blank test of the "permanganate" method[73] for the determination of molybdenum in a solution containing a known amount of molybdenum compound alone.

Ca. 0.15 g. of c.p. ammonium molybdate tetrahydrate was weighed accurately to the tenth milligram into a 250 ml. beaker. It was dissolved in 100 ml. of 5% (by volume) dilute sulfuric acid. The solution was rendered slightly pink with a drop of 10% potassium permanganate solution. The following solutions were then passed through a Jones reductor[74] in the order given at a rate of about 100 ml. per minute under slight suction: 50 ml. of 5% by volume of dilute sulfuric acid, 100 ml. of the solution to be reduced, 50 ml. of 5% by volume dilute sulfuric acid, 100 ml. of distilled water, into 50 ml. of

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[73] Ibid., pp. 307-9. [74] Ibid., pp. 108-12.

TABLE 7

Blank Tests for the Determination of Rhenium by Tetraphenylarsonium Perrhenate Method from Either 6M Ammonium Hydroxide or 5M Hycrochloric Acid, or 0.6M Tartaric Acid Solution Containing Known Amounts of Rhenium and Molybdenum

Sample, No.	1	2	3	4	5	6
Wt. of $KReO_4$, g.	0.06213	0.06213	0.2026	-	-	-
Wt. of $(NH_4)_6Mo_7O_{24}.4H_2O$, g.	0.73606	0.73607	0.06001	-	-	-
Vol. in ml. of the blank test solution	- -	- -	- -	25 No.2	25 No.2	20 No.3
Eq. wt. of rhenium, g.	0.0400	0.0400	0.130424	0.009057	0.009057	0.130424
Eq. wt. of molybdenum, g.	0.0400	0.0400	0.03261	0.081514	0.081514	0.03261
Water, ml.	0	18	0	1	21	0
Conc. NH_4OH, ml.	0	20	20	20	0	0
Conc. HCl, ml.	21	0	0	0	0	0
$(CHOHCOOH)_2.H_2O$, g.	0	0	0	0	5.05	5.05
NaCl, g.	1.46	1.46	1.46	1.46	1.46	1.46
1% Ph_4AsCl solution used, ml. (theoretically required, ml.)	29 (9+15)	12 (9)	30 (29.3)	4 (2.4)	4 (2.4)	30 (29.3)
Wt. of Ph_4AsReO_4, g.	0.1413*	0.1360	0.4300	0.0296	0.0300	0.4049
Wt. of rhenium found, g.	0.04155	0.03999	0.12644	0.8703	0.08821	0.119045
% of error	+3.9	0	-3.06	+6.76	+8.22	-8.72

*Probably the precipitate was in the form of $xPh_4AsReO_4.y(Ph_4As)_6Mo_7O_{24}$.

ferric phosphate solution (100 g. of ferric sulfate was dissolved in 500-800 ml. of distilled water; it was then added to 175 ml. of 85% phosphoric acid and 20 ml. of concentrated sulfuric acid, and diluted to 1 liter. The solution was slight pink and contained 0.14 g. of iron per milliliter).

The reduced solution was brownish in color. However, its color faded gradually when it was titrated with a standard potassium permanganate solution to the end point. A blank titration of a solution containing 200 ml. of water, 100 ml. of 5% by volume dilute sulfuric acid and 50 ml. of the ferric phosphate solution with the same standard potassium permanganate solution was done.

The data are tabulated in Table 8.

TABLE 8

Blank Tests of the Determination of Molybdenum by the "Permanganate Titration" Method from a Solution Containing a Pure Molybdenum Compound

Sample, No.	1	2
Wt. of $(NH_4)_6Mo_7O_{24}.4H_2O$, g.	0.1500	0.1500
Equivalent wt. of molybdenum, g.	0.081514	0.081514
Vol. of 0.1145N $KMnO_4$ used, ml.	23.7	24.05
Vol. of blank titration, ml.	0.1	0.1
Wt. of molybdenum found, g.	0.08313	0.08441
% of error	+1.985%	+3.55%

(d) Blank tests of the "permanganate titration" method for the determination of rhenium in a pure rhenium compound or in a mixture of rhenium and molybdenum compounds.

The Jones reductor was washed with 200-500 ml. of a warm 5% (by volume) dilute sulfuric acid followed by 100-200 ml. of cold distilled water. The air entrapped in the zinc was removed by placing water in the receiver, tightly stoppering the top of the completely filled reductor and alternately applying and releasing suction until no more gas was set free.

Dilute sulfuric acid (5% by volume) solutions containing not more than 0.06 mg.[75] of rhenium per ml. with or without an equal amount of molybdenum were prepared. A solution containing about double the amount of rhenium per ml. was also prepared for comparison.

One of the prepared solutions containing equal amounts of rhenium and molybdenum was first treated with ∝-benzoinoxime reagent solution[76] to remove its molybdenum content.

All the solutions were reduced through the Jones reductor with the same procedure described in the preceding section (c) into 50 ml. of the ferric phosphate solution.

All the reduced solutions except the one (colorless) which had been treated with ∝-benzoinoxime reagent solution were light yellow in color. The reduced solutions were titrated with 0.1145 N permanganate solution and corrected the

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[75]Hillebrand, Lundell, Bright, and Hoffman, op. cit., p. 322.

[76]Refer to section (g), page 60 of this article.

volume for that required in a blank run.

The data are summarized in Table 9.

TABLE 9

Blank Tests for the Determination of Rhenium by the "Permanganate Titration" Method from a Pure Rhenium Compound or a Mixture of Rhenium and Molybdenum Compounds

Sample, No.	1	2	3	4
Wt. of $KReO_4$, g.	0.06213	0.03106	0.03106	0.03106
Wt. of $(NH_4)_6Mo_7O_{24}.4H_2O$, g.	0	0	0.0368	0.0368
Eq.wt. of rhenium, g.	0.0400	0.0200	0.0200	0.0200
Eq.wt. of molybdenum, g.	0	0	0.0200	0.0200
Vol. of 5% dil. H_2SO_4, ml.	350	350	325	350
Vol. of α-benzoinoxime reagent solution, ml.	-	-	25	-
Content of rhenium in solution, mg./ml.	0.114	0.057	0.057	0.057
Vol. of 0.1145N $KMnO_4$ theo. required for the rhenium content, ml.	15	7.5	7.5	7.5
and the molybdenum content, ml.	0	0	0	5.45
Vol. of 0.1145N $KMnO_4$ used, ml.	12.4	7.3	6.8	12.15
% of difference, %	-16.7	-1.33	-14.7	-5.76

(e) Blank tests of the "permanganate titration" method for the determination of rhenium and molybdenum simultaneously in solutions containing a definite known amount of molybdenum with various known amounts of rhenium.

An aliquot portion of the prepared blank test solutions[77] was pipetted or appropriate amounts of $KReO_4$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ were weighed into a 250 ml. beaker. Five ml. of concentrated sulfuric acid and such amount of water as to make each 100 ml. of 5% (by volume) dilute sulfuric acid solution were added. It was pinked with a drop of 10% potassium permanganate solution and reduced through the Jones reductor as the way mentioned in section III-B-2-(c) into 50 ml. of the ferric phosphate solution. A lot of gas bubbles which was believed to be hydrogen gas, accompanied with heat, evolved in the Jones reductor when the solutions containing both rhenium and molybdenum were passed through the column. The amount of the gas and heat evolved seemed to be proportional to the amount of rhenium contained in the solution to be reduced.

The solution was then titrated with the standard potassium permanganate solution. A correction was made for the blank running.

The volume of the standard potassium permanganate solution theoretically required for the rhenium or molybdenum content was calculated according to the following equations:

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[77]Refer to p.48 of this article.

$$\text{Vol. in ml. for rhenium} = \frac{\text{Wt. of rhenium in sample, g.}}{N_{KMnO_4} \times \frac{186.31}{8,000}}$$

$$\text{Vol. in ml. for molybdenum} = \frac{\text{Wt. of molybdenum in sample, g.}}{N_{KMnO_4} \times \frac{95.95}{3,000}}$$

The data are tabulated in Table 10.

TABLE 10

Blank Tests for the Determination of Rhenium and Molybdenum Simultaneously by the "Permanganate Titration" Method from Solutions Containing a Definite Known Amount of Molybdenum with Various Known Amounts of Rhenium

Sample, No.	1	2	3
Vol. in ml. of the prepared blank test solution	50 No.1	25 No.2	- -
Wt. of $KReO_4$, g.	-	-	0.50645
Wt. of $(NH_4)_6Mo_7O_{24}.4H_2O$, g.	-	-	0.1500
Eq. wt. of molybdenum content, g.	0.081514	0.081514	0.081514
Eq. wt. of rhenium content, g.	0.081514	0.009057	0.32606
Vol. of 0.1145N $KMnO_4$ theo. required			
for rhenium, ml.	30.57	3.40	122.28
for molybdenum, ml.	22.26	22.26	22.26
in total, ml.	52.83	25.66	144.54
Vol. of 0.1145N $KMnO_4$ used, ml.	39.90	24.70	58.90

(f) Blank tests of the "permanganate titration" method for the determination of molybdenum after the precipitation of rhenium by Ph_4AsCl in a solution containing known amounts of rhenium and molybdenum.

The filtrates from the experiments of section III-B-2-(b), pages 51-52, were used for further determination of their molybdenum contents by permanganate titration method.

(1) The ammonium hydroxide solution

Since ammonical solution, which will react with mercury and render it worthless, should never be admitted in the Jones reductor, the filtrates of sample No. 2, 3, and 4, section III-B-2-(b), pages 51-52, were first neutralized with dilute sulfuric acid. However, in each case, a white precipitate which was formed by molybdenum and the excess Ph_4AsCl added was observed when the alkaline concentration of the solution was thus reduced. No further work could be done for the determination of molybdenum by permanganate titration method except redissolving the precipitate to bring back the molybdenum into solution.

(2) The tartaric acid solution

The filtrate of sample No. 5, section III-B-2-(b), pages 51-52, was first neutralized with concentrated ammonium hydroxide and concentrated sulfuric acid was added to make a solution of 5% by volume of sulfuric acid. In each case, a red precipitate, probably Ph_4AsMnO_4, was formed when the solution was added with drops of 10% potassium permanganate solution. The red precipitate was filtered off. However, the solution seemed to possess a strong reducing power since it could not be pinked even with a large amount of 10% potassium permanganate solution. A blank test was done to establish that a tartaric acid solution alone would not discolor

the permanganate solution when sulfuric acid had been added.

(3) The hydrochloric acid solution

The filtrate of sample No. 1, section III-B-2-(b), pages 51-52, was diluted with water to make a 150 ml. of 14%[78] hydrochloric acid solution. Ten per cent potassium permanganate solution was added enough to precipitate the excess Ph_4AsCl, and the red precipitate formed was filtered off. The slightly pink clear solution was then reduced in the Jones reductor by the following treatments at a rate of 50-100 ml. per minute: 50 ml. of 10% by volume hydrochloric acid, 150 ml. of the solution to be reduced, 50 ml. of 10% by volume hydrochloric acid, 100 ml. of distilled water, all were run into 50 ml. of ferric phosphate solution.

The reduced solution was yellow in color. It was treated with 30 ml. of a magnesium sulfate titration mixture and then titrated with 0.1145N potassium permanganate solution. A 7.5 ml. of the standard permanganate solution was used, which was only equivalent to 0.2747 g. of molybdenum. It further proved that the molybdenum and rhenium were coprecipitated by Ph_4AsCl solution in a hydrochloric solution.

(g) Blank test of the α-benzoinoxime method[79] for the determination of molybdenum in a solution containing known amounts of molybdenum and rhenium.

An appropriate amount (not more than 0.15 g. of

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[78] Hillebrand, Lundell, Bright, and Hoffman, op. cit., p. 110.

[79] Ibid., pp. 310-1.

molybdenum content) of the prepared blank test solution, page 48, containing known amounts of rhenium and molybdenum was pipetted into a solution of 10 ml. of concentrated sulfuric acid diluted to 200 ml. with distilled water. It was then chilled to a temperature of 5-10°C, with ice water. Ten ml. of ∝-benzoinoxime reagent solution (9 g. of ∝-benzoinoxime from Eastman Kodak Chemicals Corp. was dissolved in 450 ml. of 95% alcohol) and 5 ml. extra for each 0.01 g. of molybdenum present was added slowly to it with stirring. (Two to five times the amount of reagent required by the ratio 1 Mo to 3 $C_6H_5.CHOH.CHOH.C_6H_5$ is needed.) Bromine water was added just sufficient to tint the solution a pale yellow. (A slight excess of bromine must be present in order to counteract a tendency toward slight reduction of molybdenum with consequent incomplete precipitation.) Then 5 ml. more of the ∝-benzoinoxime reagent solution was added. The solution was allowed to remain in the cooling mixture 10 to 15 minutes with occasional stirring and then filtered through an S&S No. 597,11 cm. filter paper of average ash per circle less than 0.0003 g. with a slight suction. The filtrate was filtered again if it was not absolutely clear.

The precipitate was washed with 200 ml. of a cold freshly prepared solution containing 25-50 ml. of the prepared ∝-benzoinoxime reagent solution and 10 ml. of concentrated sulfuric acid in 1 liter. The washed precipitate together with the filter paper was transferred to a weighed platinum or porcelain crucible, cautiously dried, charred and then

ignited to constant weight at 500-525°C in an electric muffle. The molybdenum was weighed as MoO_3.

The data are summarized in Table 11.

(h) Comparison of the "α-benzoinoxime" method and the "permanganate titration" method for the determination of molybdenum in the same sample of pure molybdenum sulfide.

Ca. 0.3 g. of a dried, pulverized sample of pure molybdenum sulfide was treated with 30% H_2O_2 in alkaline solution to prepare 100 ml. of solution. Twenty-five ml. of the solution was diluted with about 150 ml. of water, neutralized with concentrated sulfuric acid (10 ml. in excess) and finally diluted to about 200 ml. Its molybdenum content was then determined by α-benzoinoxime method.

Another 25 ml. of the 100 ml. prepared solution was neutralized with concentrated sulfuric acid (5 ml. in excess) and diluted to about 100 ml. Its molybdenum content was determined by permanganate titration method. The same sample of code number RO-M100-T-As-3 (refer to Table 4, p. 36) was used. However, the determinations were done at different dates.

The data are summarized in Table 12.

(i) Blank test of the "lead molybdate"[80] method for the determination of molybdenum in a solution containing known amounts of molybdenum and rhenium.

An appropriate volume containing about 0.1 g. of molybdenum was pipetted from the prepared blank test solutions

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[80]Hillebrand, Lundell, Bright, and Hoffman, op. cit., pp. 311-3.

TABLE 11

Blank Tests for the Determination of Molybdenum by the ∝-Benzoinoxime Method from Solutions Containing Known Amounts of Molybdenum and Rhenium in Various Proportions

Sample, No.	1	2	3	4	5	6
Vol. in ml. of the prepared blank test solution	75 No. 1	75 No. 1	40 No. 2	40 No. 2	50 No. 3	50 No. 3
Molybdenum content, g.	0.12227	0.12227	0.130424	0.130424	0.81514	0.81514
Rhenium content, g.	0.12227	0.12227	0.01449	0.01449	0.32606	0.32606
Molybdenum : Rhenium	1 : 1	1 : 1	9 : 1	9 : 1	1 : 4	1 : 4
∝-Benzoinoxime reagent solution, ml.	75+5	75+5	75+5	75+5	55+5	55+5
Wt. of MoO_3, g.	0.1808	0.1815	0.1939	0.1941	0.1210	0.1218
Wt. of Molybdenum found, g.	0.1206	0.1210	0.1290	0.1291	0.08047	0.08119
% of error, %	1.39	1.06	1.07	1.07	1.23	0.39
Type of crucible used	platinum	platinum	porcelain	porcelain	porcelain	porcelain

TABLE 12

Comparison of the "α-Benzoinoxime" Method and the "Permanganate Titration" Method for the Determination of Molybdenum in a Same Sample of Pure Molybdenum Sulfide

Method	Permanganate Titration	-Benzoinoxime
Date determined	Feb. 13, 1956	March 13, 1956
Sample, code number	RO-M100-T-As-3	RO-M100-T-As-3
Wt. of sample, g.	0.3000	0.3016
Reagent for preparing solution	30%H_2O_2 in NaOH solution	30% H_2O_2 in NH_4OH solution
Wt. of residue, g.	0	0.0024
Vol. of 0.1145N $KMnO_4$, ml.	11.0	-
Wt. of MoO_3, g.	-	0.0575
Wt. of $BaSO_4$, g.	0.3357	0.3286
% of Mo determined	53.7	51.3
% of S determined	30.75	30.2
% of moisture balanced	15.55*	18.5*
% of Mo on dry basis	63.2	63.0
% of S on dry basis	36.8	37.0

*The catalyst dried to constant weight in a vacuum pistol over P_2O_5 under 50-100 microns at a temperature of about 150°C still holds certain amount of water and will absorb moisture if it is exposed to air.

(refer to p. 48) of known molybdenum and rhenium contents. About 1 ml. of 6N sulfuric acid was added to it such that the solution would contain about 0.3 g. of sulfate ion which

might be present through the solution of molybdenum trisulfide. It was treated with ammonium hydroxide in slight excess and then made to slightly acidic with acetic acid. After adding 25. ml. of a 50% solution of ammonium acetate, the solution was diluted to 200 ml., heated to and kept near boiling. A lead acetate reagent solution was added to it drop by drop from a burette with constant stirring until the precipitation was complete. The lead acetate reagent solution was prepared by dissolving 40 g. of $Pb(Ac)_2.3H_2$),M.W.379.35, in one liter of 1% acetic acid solution. Each ml. of the solution contained 0.04 g. of $Pb(Ac)_2.3H_2O$. The complete precipitation was tested by withdrawing a drop of the solution and testing with a freshly prepared 0.5% solution of tannic acid. A yellow color indicated the precipitation was not complete while colorless indicated it was. After digesting on a steam plate for 1/2-1 hour, the solution was filtered through a weighed Gooch crucible. The precipitate was decanted 3 to 4 times with 75 ml. portions of hot 2-3% solution of ammonium nitrate and then transferred to the Gooch crucible, washed with water until soluble salts had been removed. The Gooch crucible with the content was cautiously dried and ignited to constant weight at 800-900°C in an electrical muffle. The precipitate was weighed as $PbMoO_4$.

The data are summarized in Table 13.

TABLE 13

Blank Tests for the Determination of Molybdenum by the "Lead Molybdate" Method from Solutions Containing Known Amounts of Molybdenum and Rhenium

Sample, No.	1	2	3	4	5	6
Vol. in ml. of the prepared blank test solution	75 No.1	75 No.1	40 No.2	40 No.2	50 No.3	50 No.3
Molybdenum content, g.	0.12227	0.12227	0.130424	0.130424	0.081514	0.081514
Rhenium content, g.	0.12227	0.12227	0.01449	0.01449	0.32606	0.32606
Molybdenum : rhenium	1 : 1	1 : 1	9 : 1	9 : 1	1 : 4	1 : 4
Conc. H_2SO_4, ml.	0	0.22	0	0.23	0	0.15
50% NH_4Ac solution, ml.	0	25	25	25	25	25
Water, ml.	175	150	185	185	175	175
Vol. of lead acetate reagent solution actually used, ml. (theo. required, ml.)	11.5 (12)	12.7 (12)	13.0 (13)	13.1 (13)	8.5 (8)	8.0 (8)
Wt. of $PbMO_4$, g.	0.4579	0.4658	0.4942	0.4934	0.3108	0.3090
Wt. of molybdenum found, g.	0.11967	0.12173	0.12915	0.1290	0.08122	0.080733
% of error, %	2.12	0.44	0.97	0.986	0.356	0.956

3. Analyses of the Catalysts Prepared

The catalysts were brought into solution by 30% H_2O_2 in either 5N NH_4OH or 5N NaOH (for pure molybdenum sulfide only) solution.

The molybdenum content in pure molybdenum sulfide was either determined by permanganate titration method (in most cases) or by α-benzoinoxime method. The molybdenum content in mixtures of rhenium and molybdenum sulfides was determined by α-benzoinoxime method.

The rhenium content in either pure rhenium sulfide or mixtures of rhenium and molybdenum sulfides was determined by tetraphenylarsonium perrhenate method using tetraphenylarsonium chloride as precipitating reagent in a 6M ammonium hydroxide solution.

The sulfur content of all the catalysts was determined by the barium sulfide method with a general procedure as follows:

An aliquot amount of the prepared solution was pipetted into a 600 ml. beaker and diluted with 300-350 ml. of distilled water (each 100 ml. of the solution contained less than 0.020-0.025 g. of sulfur as sulfate). It was neutralized with concentrated hydrochloric acid with 2 ml. in excess, heated to boiling, and treated slowly with 10 ml. of 10% $BaCl_2.2H_2O$ solution with vigorous stirring, and then digested on a steam plate overnight. The precipitate was filtered into a weighed Gooch crucible, washed with hot water until free from chloride, dried to constant weight at 120°C in an electric

oven and weighed as $BaSo_4$.

(a) Analyses of the pure molybdenum sulfides prepared from various conditions.

Exactly 0.3000 g. of a dry, pulverized sample was weighed into a 100 ml. beaker. It was treated with 5 ml. of 5 N NaOH solution. The beaker was covered with a watch glass and let stand for several hours. Then 30% H_2O_2 was added to it in 0.5 ml. portions with shaking and occasional cooling until the solution turned from reddish brown to yellow, light green, and finally to colorless. A total amount of 3-5 ml. of 30% H_2O_2 was used. The solution was heated to near boiling on a steam plate to destroy the excess hydrogen peroxide. Any insoluble matter was filtered off and dried to constant weight at 110°C. The colorless solution was diluted to 100 ml. in a volumetric flask. Fifty ml. of the solution was pipetted into a 600 ml. beaker and its sulfur content was determined by the barium sulfate method described in the preceding paragraph.

Twenty-five ml. of the solution was pipetted into a 400 ml. beaker for the determination of molybdenum content either by permanganate titration method or by the α-benzoinoxime method.

The data are tabulated in Table 14. Most of the determinations of molybdenum were done by permanganate titration method except as indicated.

TABLE 14

Compositions of the Pure Molybdenum Sulfide Catalysts Prepared

Sample	Code Number	Wt. of residue, g. (% of sample)	Wt.of $BaSO_4$ g.	Vol. of 0.1145N $KMnO_4$,ml.	% Sulfur determined	% Molybdenum determined	% H_2O (the remainder)	% Sulfur dry basis	% Molybdenum dry basis
1.	RO-M100-Ah-N5-1	0	0.5361	8.3	49.1	41.1	9.8	54.4	45.6
2.	RO-M100-Ah-N5-2	0	0.5156	9.1	47.2	44.5	8.3	51.5	48.5
3.	RO-M100-Ah-N3-1	0	0.4469	9.55	40.9	46.7	12.4	46.8	53.2
4.	RO-M100-Ah-N3-2	0	0.3177	10.6	29.1	51.8	19.1	35.9	64.1
5.	RO-M100-Ah-N2.5-4*	0	0.4861	0.0505 (Wt.of MoO_3)	44.51	44.87	10.62	49.75	50.25
6.	RO-M100-Ah-N1-2	0	0.4106	10.4	37.65	50.8	11.55	42.5	57.5
7.	RO-M100-Ah-NO.3-1	0	0.4140	10.55	38.0	51.6	10.4	42.4	57.6
8.	RO-M100-Ah-NO.3-2	0	0.3858	10.25	35.3	50.1	14.6	41.3	58.7
9.	RO-M100-Ah-NO.25-1	0	0.4425	10.30	40.6	50.3	9.1	44.6	55.4
10.	RO-M100-As-NO.5-1	0	0.3269	10.9	30.0	53.2	16.8	36.0	64.0
11.	RO-M100-W-NO-1	0.0195 (6.5%)	0.4831	9.6	47.3	50.1	2.6	48.6	51.4
12.	RO-M100-Ba-NO.25-1	0	0.4114	8.05	37.7	39.4	22.9	48.9	51.1
13.	RO-M100-Ba-NO.25-2	0	0.4983	9.0	45.7	44.0	10.3	50.9	49.1

TABLE 14--Continued

Sample	Code Number	Wt. of residue, g. (% of sample)	Wt.of $BaSO_4$ g.	Vol. of 0.1145N $KMnO_4$, ml.	% Sulfur determined	% Molybdenum determined	% H_2O (the remainder)	% Sulfur dry basis	% Molybdenum dry basis
14.	RO-M100-Ba-N2.5-1	0	0.5348	9.0	49.0	44.0	7.0	52.7	47.3
15.	RO-M100-Ba-N2.5-4*	0	0.5448	0.0502 (Wt.of MoO_3)	49.89	44.61	5.5	52.8	47.2
16.	RO-M100-Ba-N5-1	0.0134 (4.47%)	0.5357	9.05	51.25	46.2	2.55	52.6	47.4
17.	RO-M100-T-As-2	0	0.2361	11.8	21.65	57.6	20.75	27.4	74.6
18.	RO-M100-T-As-3	0	0.3357	11.0	30.75	53.7	15.55	36.8	63.2

Composition of MoS_3: Mo=49.94% S=50.06%. Composition of MoS_2: Mo=59.94% S=40.06%.

*The molybdenum content was determined by the α-benzoinoxime method.

(b) Analyses of the pure rhenium sulfides prepared from various conditions.

Ca. 0.3 g. of a dry, pulverized sample was weighed accurately to the tenth milligram into a 100 ml. beaker. It was treated with 10 ml. of 5N NH_4OH solution and 6-9 ml. of 30% H_2O_2 with the same procedure described in section (d), page 47. Any residue was filtered into a weighed Gooch crucible, followed by washing with water and drying to constant weight at 110°C. The combined filtrate and washings were then diluted to 100 ml. in a volumetric flask. Fifty ml. of the solution was pipetted for the determination of sulfur content by the barium sulfate method. The sulfur content of the original sample was calculated according to the following equation:

$$\% \text{ of } S = \frac{2 \times BaSO_4 \times \frac{32.06}{233.42}}{W - r} \times 100$$

wherein W is for the weight of sample and r is for that of residue.

Twenty ml. of the solution was pipetted into a 125 ml. conical flask and its rhenium content was determined by tetraphenylarsonium perrhenate method from a 6M NH_4OH solution. The rhenium content of the sample was calculated according to the following equation:

$$\% \text{ of rhenium} = \frac{5 \times Ph_4AsReO_4 \times \frac{186.31}{633.62}}{W - r} \times 100$$

The data are tabulated in Table 15.

TABLE 15

Compositions of the Pure Rhenium Sulfide Catalysts Prepared

Sample	Code Number	Wt. of sample, g.	Wt. of residue, g. (% of sample)	Wt. of ppt., g. R for Ph_4AsReO_4 B for $BaSO_4$	% Determined Re=rhenium S =sulfur H_2O(the remainder)	% Dry Basis (% Calculated) Re=62.41% S=37.59%
1.	R100-MO-Ah-N6-1	0.2411	0	R=0.0885 B=0.2168	Re=53.9 S =24.8 H_2O=21.3	Re=68.5 S =31.5
2.	R100-MO-Ah-N5-1	0.3007	0	R=0.1190 B=0.2900	Re=58.1 S =26.5 H_2O=15.4	68.7 31.3
3.	R100-MO-Ah-NO.25-1	0.3011	0	R=0.1293 B=0.3920	Re=63.13 S =35.71 H_2O= 1.16	63.8 36.2
4.	R100-MO-Ba-NO.25-1	0.2999	0	R=0.1249 B=0.3865	Re=61.23 S =35.40 H_2O= 3.37	62.34 37.66
5.	R100-MO-Ba-N5-1	0.3009	0	R=0.1269 B=0.2772	Re=62.0 S =25.3 H_2O=12.7	71.0 29.0
6.	R100-MO-T-As-3	0.3018	0.0056 (1.85%)	R=0.1153 B=0.2928	Re=57.3 S =27.1 H_2O=15.6	67.9 32.1
7.	R100-MO-T-As-4	0.3016	0	R=0.1156 B=0.3834	Re=56.5 S =34.9 H_2O= 8.6	61.8 38.2

(c) Analyses of mixtures of rhenium and molybdenum sulfides of various compositions prepared.

Ca. 0.5 g. of a dry, pulverized sample was weighed accurately to the tenth milligram into a 100 ml. beaker. The solution was prepared by treating it with an appropriate amount of 30% H_2O_2 and 5N NH_4OH (refer to Table 16). Any residue was filtered into a weighed sintered glass crucible, followed by drying to constant weight at 110°C. The solution was then diluted with distilled water to 100 or 50 ml. in a volumetric flask according to the relative proportion of rhenium sulfide to molybdenum sulfide in the sample (refer to Table 16). Twenty ml. each of the solutions prepared was pipetted into a 125 ml. conical flask and its rhenium content was determined by the tetraphenylarsonium perrhenate method in a 6M NH_4OH solution. Ten ml. each of the solutions prepared was used for the determination of its sulfur content by the barium sulfate method. An aliquot portion (refer to Table 16) of the solutions prepared was used for the determination of its molybdenum content by the ∝-benzoinoxime method.

Suggested amounts of various reagents used for the determinations of the constituents are listed in Table 16.

The analytical data for the mixtures of rhenium and molybdenum sulfides of various compositions are summarized in Table 17.

TABLE 16

Suggested Amounts of Reagents Used for the Determinations of Molybdenum, Rhenium and Sulfur from 0.5 g.(ca.) of Mixtures of Molybdenum and Rhenium Sulfides

Sample: Re_2S_7/MoS_3	80/20	50/50	20/80
Wt. of sample taken, g.	0.5	0.5	0.5
Eq. wt. of Re_2S_7, g.	0.4	0.25	0.1
Eq. wt. of MoS_3, g.	0.1	0.25	0.4
Eq. wt. of rhenium content, g.	0.25(50%)	0.156(31.2%)	0.0625(12.5%)
Eq. wt. of molybdenum content, g.	0.05(10%)	0.124(24.8%)	0.20(40%)
Eq. wt. of sulfur content, g.	0.20(40%)	0.22(44%)	0.2375(47.5%)
Volume of solution prepared, ml.	100	100	50
Volume in ml. of the solution pipetted for the determination of:			
Rhenium (rhenium content, g.)	20(0.05)	20(0.031)	20(0.025)
Sulfur (sulfur content, g.)	10(0.02)	10(0.022)	10(0.0475)
Molybdenum (molybdenum content, g.)	70(0.035)	50(0.0625)	10(0.04)
Reagents used:			
5N NH_4OH, ml.			
theo. required	2.27	2.48	2.71
suggested	5-10	5-10	5-10
30% H_2O_2, ml.			
theo. required	2.44	2.66	2.99
suggested	5-10	5-10	5-10

TABLE 16--Continued

Sample: Re_2S_7/MoS_3	80/20	50/50	20/80
Reagents used:			
10%$BaCl_2.2H_2O$, ml.			
theo. required	1.6	1.7	3.7
suggested	6	6	10
1%Ph_4AsCl, ml.			
theo. required	11.3	7.0	5.65
suggested	16	11	9
α-benzoinoxime reagent soln., ml.			
optimum	27.5+5	43+5	30+5
suggested	50+5	60+5	50+5

C. Catalytic Hydrogenation

General procedure: A weighed glass liner containing the substrate (usually 0.2 mole) to be reduced, a catalyst (usually 2.5 g. per mole of substrate), with or without a solvent or diluent (usually 20 ml. of ethanol) was weighed and placed in a hydrogenation autoclave, which was then charged with hydrogen under an initial pressure of 3000 psi at room temperature. A 2-5°C of temperature rise was observed when the hydrogen pressure was built up to 3000 psi. It required about 5 minutes or less of standing to bring the temperature back to the original temperature. In most cases an Aminco rocking type autoclave of a fixed rocking speed of 37 cycles per minute was used. In a few cases a Magne-Dash (Autoclave Engineering, Inc.) apparatus which has variable agitation was operated at ca. 35-40 cycles per minute. After standing for

TABLE 17

Compositions of the Mixtures of Molybdenum and Rhenium Sulfides Prepared from Various Conditions

Sample	Code Number	Wt. of sample, g.	Wt. of residue, g. (% of sample)	Wt. of ppt., g. R for Ph_4AsReO_4 B for $BaSO_4$ M for MoO_3	% Determined Re=rhenium S =sulfur Mo=molybdenum H_2O(the remainder)	% Dry Basis (% Calculated)
1.	R80-M20-Ah-N5-2	0.5046	0.0010 (0.20%)	R=0.1644 B=0.1124 M=0.0410	Re=47.99 S =30.66 Mo= 7.75 H_2O=13.6	55.5 (50.0) 35.5 (40.0) 9.0 (10.0)
2.	R80-M20-Ah-N2.5-4	0.5004	0.0003 (0.06%)	R=0.1823 B=0.1359 M=0.0389	Re=53.59 S =37.32 Mo= 7.41 H_2O= 1.68	54.5 (50.0) 38.0 (40.0) 7.5 (10.0)
3.	R80-M20-Ah-N0.25-3	0.4998	0.1004 (20.1%)	R=0.1342 B=0.1030 M=0.0515	Re=49.40 S =35.42 Mo=12.28 H_2O= 2.90	50.7 (50.0) 36.7 (40.0) 12.6 (10.0)
4.	R80-M20-Ba-N0.25-3	0.5005	0.0128 (2.55%)	R=0.1564 B=0.1303 M=0.0522	Re=47.15 S =36.70 Mo=10.29 H_2O= 5.86	50.1 (50.0) 39.0 (40.0) 10.9 (10.0)
5.	R80-M20-Ba-N2.5-4	0.5002	0.0190 (3.80%)	R=0.1401 B=0.1522 M=0.0433	Re=42.80 S =43.44 Mo= 8.27 H_2O= 5.49	45.30 (50.0) 45.95 (40.0) 8.75 (10.0)

TABLE 17--Continued

Sample	Code Number	Wt. of sample, g.	Wt. of residue, g. (% of sample)	Wt. of ppt., g. R for Ph_4AsReO_4 B for $BaSO_4$ M for MoO_3	% Determined Re=rhenium S =sulfur Mo=molybdenum H_2O(the remainder)	% Dry Basis (% Calculated)
6.	R80-M20-Ba-N5-1	0.5000	0.0011 (0.22%)	R=0.1551 B=0.1308 M=0.0438	Re=45.71 S =36.01 Mo= 8.36 H_2O= 9.92	50.7 (50.0) 40.0 (40.0) 9.3 (10.0)
7.	R80-M20-T-As-1	0.5024	0.0016 (0.32%)	R=0.1604 B=0.0905 M=0.0311	Re=47.09 S =24.82 Mo= 5.91 H_2O=22.18	60.5 (50.0) 31.9 (40.0) 7.6 (10.0)
8.	R80-M20-T-As-3	0.4993	0.0002 (0.04%)	R=0.1523 B=0.1358 M=0.0472	Re=44.86 S =37.285 Mo= 9.005 H_2O= 8.85	49.1 (50.0) 40.9 (40.0) 10.0 (10.0)
9.	R50-M50-Ah-N5-2	0.4993	0.0013 (0.26%)	R=0.1094 B=0.1352 M=0.0760	Re=32.30 S =37.29 Mo=20.35 H_2O=10.06	35.9 (31.2) 41.5 (44.0) 22.6 (24.8)
10.	R50-M50-Ah-N2.5-4	0.5001	0.0021 (0.42%)	R=0.1139 B=0.1440 M=0.0810	Re=33.63 S =39.71 Mo=21.68 H_2O= 4.98	35.4 (31.2) 41.7 (44.0) 22.9 (24.8)
11.	R50-M50-Ba-N2.5-4	0.5005	0.0116 (2.32%)	R=0.0922 B=0.1471 M=0.0769	Re=27.73 S =41.33 Mo=20.97 H_2O= 9.97	30.8 (31.2) 45.9 (44.0) 23.3 (24.8)

TABLE 17--Continued

Sample	Code Number	Wt. of sample, g.	Wt. of residue, g. (% of sample)	Wt. of ppt., g. R for Ph_4AsReO_4 B for $BaSO_4$ M for MoO_3	% Determined Re=rhenium S =sulfur Mo=molybdenum H_2O(the remainder)	% Dry Basis (% Calculated)
12.	R50-M50-Ba-N5-1	0.5009	0.0009 (0.02%)	R=0.1004 B=0.1486 M=0.0861	Re=28.78 S =40.82 Mo=22.96 H_2O= 7.44	31.1 (31.2) 43.1 (44.0) 25.8 (24.8)
13.	R50-M50-T-As-1	0.5007	0.0059 (1.18%)	R=0.1403 B=0.0845 M=0.0384	Re=41.69 S =24.00 Mo=10.59 H_2O=23.72	54.7 (31.2) 31.5 (44.0) 13.8 (24.8)
14.	R50-M50-T-As-3	0.5015	0.0022 (0.44%)	R=0.1020 B=0.1247 M=0.0742	Re=30.05 S =34.32 Mo=19.82 H_2O=15.81	35.70 (31.2) 40.70 (44.0) 23.60 (24.8)
15.	R20-M80-Ah-N5-2	0.4990	0.0014 (0.28%)	R=0.1285 B=0.2798 M=0.0369	Re=18.985 S =38.615 Mo=24.71 H_2O=17.69	23.1 (12.5) 46.9 (47.5) 30.0 (40.0)
16.	R20-M80-Ah-N2.5-4	0.4989	0.0109 (2.20%)	R=0.1142 B=0.2937 M-0.0431	Re=17.20 S =40.21 Mo=29.44 H_2O=13.15	19.8 (12.5) 46.3 (47.5) 33.9 (40.0)
17.	R20-M80-Ba-N2.5-4	0.5006	0.0018 (0.36%)	R=0.0807 B=0.3260 M=0.0514	Re=11.89 S =44.69 Mo=34.34 H_2O= 9.08	13.0 (12.5) 49.2 (47.5) 37.8 (40.0)
18.	R20-M80-Ba-N5-1	0.4991	0.0023 (0.46%)	R=0.0791 B=0.3231 M=0.0508	Re=11.74 S =44.66 Mo=34.08 H_2O= 9.52	13.0 (12.5) 49.4 (47.5) 37.6 (40.0)

TABLE 17--Continued

Sample	Code Number	Wt. of sample, g.	Wt. of residue, g. (% of sample)	Wt. of ppt., g. R for Ph_4AsReO_4 B for $BaSO_4$ M for MoO_3	% Determined Re=rhenium S =sulfur Mo-molybdenum H_2O(the remainder)	% Dry Basis (% Calculated)
19.	R20-M80-T-As-1	0.5022	0.0086 (1.72%)	R=0.1750 B=0.1704 M=0.0564	Re=26.03 S =23.71 Mo=38.08 H_2O=12.18	29.6 (12.5) 27.0 (47.5) 43.4 (40.0)
20.	R20-M80-T-As-2	0.5000	0.0089 (1.78%)	R=0.0897 B=0.0979 M=0.0482	Re=13.42 S =13.78 Mo=32.71 H_2O=40.09	22.4 (12.5) 23.0 (47.5) 54.6 (40.0)
21.	R20-M80-T-As-3	0.4992	0.0126 (2.52%)	R=0.0856 B=0.2389 M=0.0548	Re=12.93 S =33.72 Mo=37.53 H_2O=15.82	15.4 (12.5) 40.0 (47.5) 44.6 (40.0)
22.	R68-M32-Ah-N6-1*	-	-	-	Re=43.22 S =35.70 Mo=10.11 H_2O=10.97	48.5 (42.44) 40.1 (41.75) 11.4 (15.98)
23.	R40-M60-Ah-N6-1*	-	-	-	Re=24.34 S =40.14 Mo=33.24 H_2O= 2.28	24.9 (24.97) 41.1 (45.07) 34.6 (29.96)
24.	R18-M82-Ah-N6-1*	-	-	-	Re=11.37 S =45.38 Mo=36.19 H_2O= 7.06	12.2 (11.36) 48.8 (47.79) 39.0 (40.85)

*For the analyses of those catalysts, different samples were taken for the determination of their sulfur content, rhenium and molybdenum contents. Since the molybdenum was determined by the permanganate titration method after the precipitation of rhenium with tetraphenylarsonium chloride reagent solution, the data may be less correct than those of others.

10 to 30 minutes for testing of leakage, the autoclave was started rocking and heated by a heating device to a certain temperature and kept that temperature through the help of an automatic voltage controller or a variable transformer. When the desired time was due, the autoclave was stopped rocking and cooled down to the initial temperature in order to get the % of pressure drop on the basis of the theoretical pressure drop. The theoretical pressure drop was calculated by the following equation:

$$\Delta P = \frac{NxRxT}{V - v}$$

wherein ΔP is in psi, N is the number of moles of hydrogen required to reduce one mole of the substrate, T is the absolute temperature, V is the volume in liters of autoclave including the glass liner. It was 0.390 liter for Aminco rocking type autoclave, and ca. 0.20 liter for the Magne-dash apparatus; v is the volume in liters of the substrate, catalyst, and solvent, if any. Then the gas constant R would have a numerical value of 1.206. If there was no leakage in the apparatus, this calculated % of pressure drop would nearly check the % of reduction determined by subsequent analysis of the hydrogenated product.

The autoclave was then released from the hydrogen gas. The glass liner with its content was taken out and weighed. A % of recovery of hydrogenation was thus calculated. The analyses of hydrogenated products, which depend upon the substrates used, will be stated in a separate section later.

For the comparison of the catalytic activity of the catalysts of various compositions, a mixture of rhenium heptasulfide and molybdenum trisulfide with the composition ratio of 80:20 was first used as catalyst for hydrogenation of a certain reducible substrate. A minimal working temperature was found such that the pressure change in the autoclave versus time would show a smooth curve on the automatic recording chart. An appropriate interval of time was taken such that the total pressure drop would be about 80% of the theoretical value calculated. This average working temperature and time interval as well as an initial pressure of 3000 psi were then chosen as working conditions for the hydrogenation of the same substrate with catalysts of other various compositions, pure sulfides as well as those ones of the ratio of 50:50 and 20:80.

Nitrobenzene, styrene, and cyclohexanone were chosen as examples for the three representative reducible organic groups, i.e., nitro group, carbon to carbon double bond conjugated with a benzene ring, and carbon to oxygen double bond as substrates. The procedures of the analyses of their hydrogenated products are as follows:

1. Analyses of the hydrogenated products of nitrobenzene.

The catalyst was filtered off through a fine sintered glass crucible. The clear, usually reddish colored filtrate was stripped free of the ethanol on a water bath. The liquid mixture remaining in the distilling flask was weighed for checking the % of recovery.

Three methods for the determination of the % of hydrogenation (or the % by weight of aniline in the mixture) were considered and blank tests performed.

(a) A blank test of the "refractometrical method."

A mixture of 10 ml. each of nitrobenzene and aniline, both of reagent grade from Eastman Kodak Company, was prepared; and its refractive index was determined to be 1.5673 at 20°C with a Bausch & Lomb "56" Abbe' refractometer. (The R.I. of pure nitrobenzene was found to be 1.5518 [I.5529[81]] and that of pure aniline, 1.5851 [I.5863[81]]). The mixture was treated with 20 ml. of ethanol and 7.6 ml. of distilled water. The ethanol was stripped off at 74-78°C and water at 94-96°C in a 150 ml. claisen distilling flask. However, aniline was co-distilled over in considerable amount with water even in appreciable amount with ethanol. The remaining liquid mixture was found to have a R.I. of 1.5653 at 20°C instead of 1.5673. Therefore, this method is not practicable; besides there might be by-products such as nitrosobenzene, phenylhydroxylamine, etc., produced due to side reactions in the hydrogenation of nitrobenzene.

(b) A blank test of the "solubility method."

Since the M.P. of nitrobenzene is 5.7°C and its solubility in water at 20°C is 0.19 parts per 100 parts of water, it seemed possible to separate nitrobenzene from aniline in a cooled hydrochloric acid solution. A mixture of 10 ml. each

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[81] "Fine Organic Chemicals Catalog No. 9," Brothers Chemical Co., Orange, N.J.

of nitrobenzene and aniline, both of reagent grade, together with 7.6 ml. of water was cooled to 6-10°C. About 50 ml. of 10% dilute hydrochloric acid was added. The heavier, oily nitrobenzene layer was separated into a 10 ml. graduated cylinder. The recovered nitrobenzene was 9.6 ml., which made a 96% recovery. The aniline hydrochloride solution was evaporated to dryness on a steam plate. A 14.12 g. of white aniline monohydrochloride was obtained, which was equivalent to 10.15 g. of pure aniline. The % of recovery of aniline was thus 99%.

(c) A blank test of the "chemical extraction method."

A mixture of 10 ml. each of nitrobenzene (12.2 g.) and aniline (10.22 g.), both of reagent grade, together with 7.6 ml. of water was prepared. About 50 ml. of 10% hydrochloric acid was added with good mixing. The nitrobenzene was then extracted with 20-50 ml. of ethyl ether. The ethereal layer was separated and dried with anhydrous magnesium sulfate and then stripped of ether. The remaining nitrobenzene was weighed and its refractive index was checked. Recovered nitrobenzene (11.6 g.) made a 95% of recovery. The aqueous portion of aniline hydrochloride was neutralized with 5 N sodium hydroxide solution in excess. The aniline separated and floated on the top when the solution was in strong alkalinity and showed a white turbidity. It was extracted with appropriate amount (usually 20-50 ml.) of ether. The ethereal layer was separated, dried and stripped of ether as in the recovery of nitrobenzene. The recovered aniline was weighed and its refractive

index was checked. A 10.2 g. made it a 100% recovery.

2. Analyses of the hydrogenated products of styrene.

The hydrogenated product was transferred to a distilling flask. Two fractions of distillate were collected separately. The lower boiling point fraction of a temperature range from 74°C up to 130°C contained all the ethanol and a small amount of ethylbenzene sometimes with styrene. The ethylbenzene and styrene co-distilled with ethanol might be recovered by diluting the distillate with a large amount of water. The higher boiling point fraction from 130°C up to 140°C should be a binary mixture of styrene and ethylbenzene (the B.P. of styrene is 145.2°C, and that of ethylbenzene is 136.2°C). Its composition was found from the curve in Fig. 5 through the determination of the refractive index. The residue in the distilling flask corrected for the weight of catalyst would be a measure of polystyrene formed.

The refractive index curve of mixtures of styrene and ethylbenzene was made according to the following data:

Styrene (stabilized with tert-butylcatechol) was obtained from Eastman Kodak Company as was the ethylbenzene. The sp. gr. of styrene was taken as 0.906 at 20°C and that of ethylbenzene as 0.867.

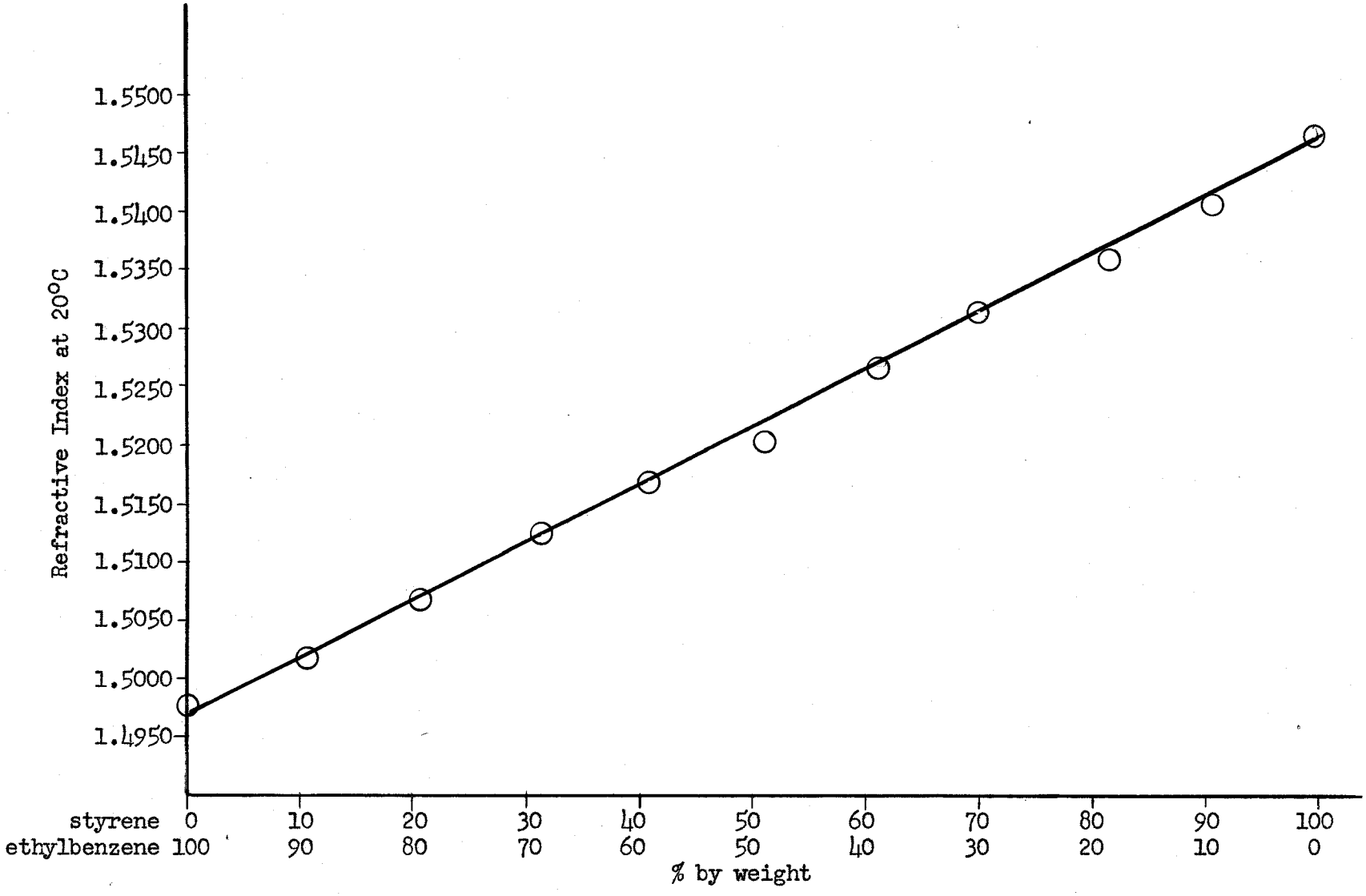


Fig. 5.--Refractive Index Curve of the Binary Mixtures of Styrene and Ethylbenzene (Determined with Bausch & Lomb "56" Abbe' Refractometer).

% by Volume		Corresponding % by Weight		Refractive Index found at 20°C (Literature[81])
Styrene	Ethyl-benzene	Styrene	Ethyl-benzene	
0	100	0	100	1.4973 (1.4959)
10	90	10.4	89.6	1.5019
20	80	20.7	79.3	1.5070
30	70	30.8	69.2	1.5127
40	60	41.1	58.9	1.5171
50	50	51.1	48.9	1.5210
60	40	61.0	39.0	1.5270
70	30	70.9	29.1	1.5319
80	20	80.7	19.3	1.5362
90	10	90.4	9.6	1.5412
100	0	100	0	1.5462 (1.5469)

3. Analyses of the hydrogenated products of cyclohexanone.

The hydrogenated product was filtered free of the catalyst through a fine sintered glass crucible. Since no solvent had been used, the clear filtrate was a binary mixture of cyclohexanone and cyclohexanol. The % of reduction or the % of cyclohexanol was found from the curve in Fig. 6 through the determination of the refractive index of the mixture.

The curve in Fig. 6 was made according to the following data:

Cyclohexanone was obtained from Matheson Company; cyclohexanol was prepared by the author from the hydrogenation of cyclohexanol under an avg. pressure of 3650 psi at an avg.

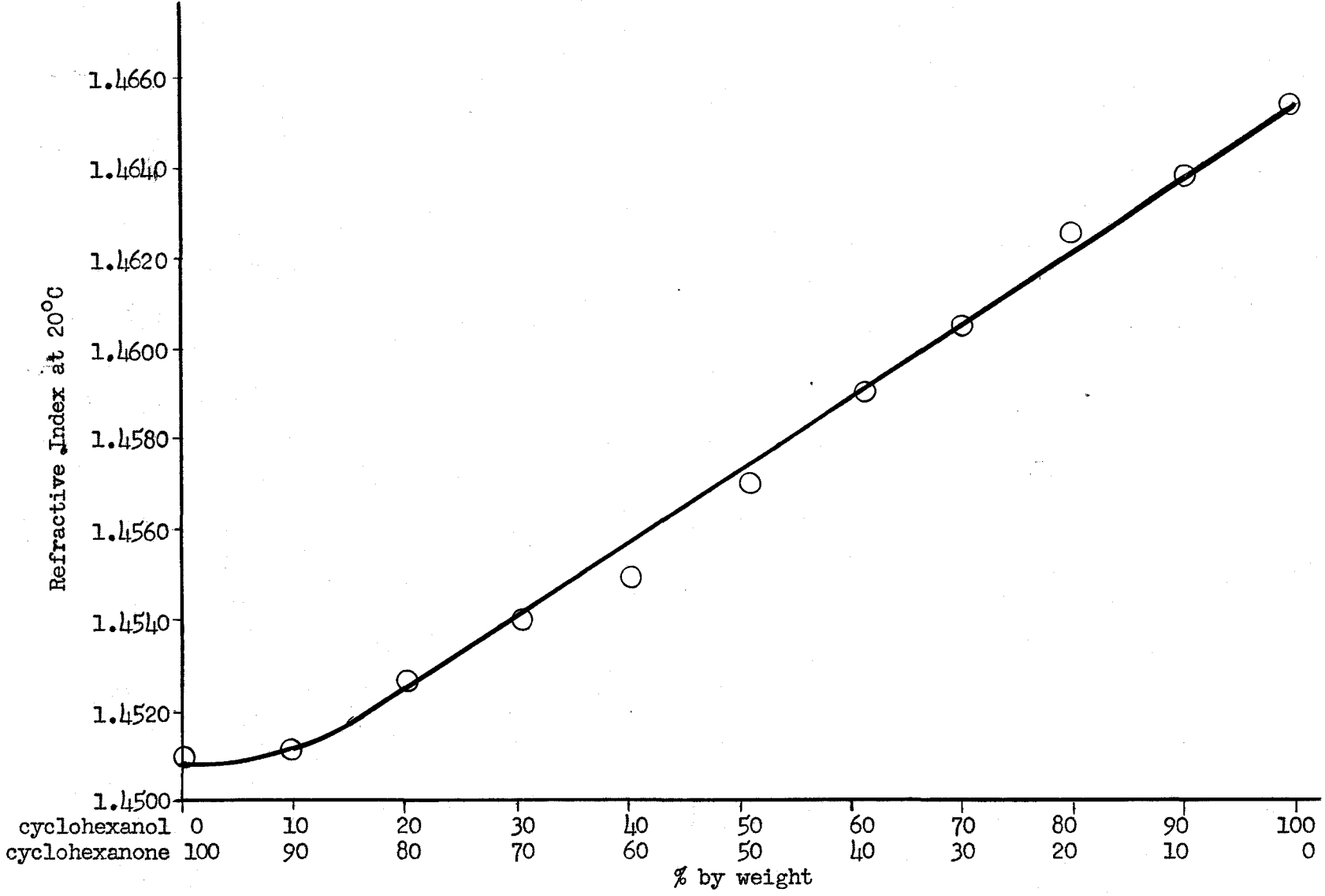


Fig. 6.--Refractive Index Curve of the Binary Mixtures of Cyclohexanone and Cyclohexanol (Determined with Bausch & Lomb "56" Abbe' Refractometer).

temperature of 115°C for about 1.33 hours. The sp. gr. of cyclohexanone was taken as 0.947 at 20°C and that of cyclohexanol as 0.962.

% by Volume		Corresponding % by Weight		Refractive Index found at 20°C (Literature[81])
Cyclohexanone	Cyclohexanol	Cyclohexanone	Cyclohexanol	
0	100	0	100	1.4655 (1.4654)
10	90	9.9	90.1	1.4638
20	80	19.9	80.1	1.4625
30	70	29.6	70.4	1.4602
40	60	39.6	60.4	1.4587
50	50	49.6	50.4	1.4570
60	40	59.6	40.4	1.4551
70	30	69.6	30.4	1.4540
80	20	79.8	20.2	1.4526
90	10	90.0	10.0	1.4511
100	0	100	0	1.4508 (1.4507)

The data for catalytic hydrogenation of nitrobenzene with pure rhenium heptasulfide, pure molybdenum sulfide, and various mixtures of them as catalysts are summarized in Table 18.

The data for catalytic hydrogenation of nitrobenzene with rhenium heptasulfide (code number R100-MO-Ah-NO.25-1) and molybdenum sulfide (code number RO-M100-Ah-N2.5-4) mixed in various proportions as catalysts are summarized in Table 19.

The data for catalytic hydrogenation of styrene with

various catalysts are summarized in Table 20.

The data for catalytic hydrogenation of cyclohexanone with various catalysts are summarized in Table 21.

TABLE 18

Hydrogenation of Nitrobenzene (usually 0.2 mole) in Ethanol (usually 20 ml.) with Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts (2.5 g. per mole of substrate)

Batch No.	Catalyst Code Number	Initial pres. psi	Initial temp. °C	Conditions of Hydrogenation Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield (Aniline)
1.	None	3000	25	145	4020	12	0
2.	RO-M100-Ah-N2.5-4	3000	25	74	3350	4.0	0*
3.	RO-M100-Ah-NO.25-1	2930	18	156	3450	11	100
4.	RO-M100-W-NO-1	3030	48	197	3820	17	100
5.	RO-M100-Ba-NO.25-1	2975	30	105	3450	3.5	23*
6.	RO-M100-Ba-NO.25-2	3010	31	114	3330	2.0	5
7.	RO-M100-Ba-NO.25-2	2970	41	153	3000	8.5	35
8.	RO-M100-Ba-N2.5-1	3070	33	117	3270	3.5	47*
9.	RO-M100-Ba-N2.5-4	2920	26	59	3200	2.7	0*
10.	RO-M100-Ba-N5-1	2990	35	105	3270	3.5	17*
11.	RO-M100-T-As-3	3000	27	73	2900	1.33	0*#
12.	RO-M100-T-As-3	3000	27	107	3700	12.0	14*#
13.	RO-M100-T-As-3	3000	27	150-175	3860	12.0	94.5*#
14.	R100-MO-Ah-N5-1	2985	31	160	3100	6	100*(without agitation)
15.	R100-MO-Ah-N5-1	3000	33	120	2650	0.35	100*

TABLE 18--Continued

Batch No.	Catalyst Code Number	Initial pres. psi	Initial temp. °C	Conditions of Hydrogenation Avg. temp. °C	Avg. pres. psi	Time hrs.	% ◊ Yield (Aniline)
16.	R100-M0-Ah-N0.25-1	3000	22	64	3200	4	38
17.	R100-M0-Ba-N0.25-1	3000	23	50	2850	2.7	100
18.	R100-M0-T-As-4	3000	23	73	3190	1.33	99
19.	R80-M20-Ah-N5-2	2990	31	46	2700	3.5	99
20.	R80-M20-Ah-N5-2	3010	28	87(→170)	3300 (→2800)	0.05	100
21.	R80-M20-Ah-N2.5-4	3000	21	46	3160	2.7	11
22.	R80-M20-Ah-N2.5-4	3000	26	55	2990	5.0	61
23.	R80-M20-Ah-N2.5-4	3000	27	57	3000	6.0	76
24.	R80-M20-Ah-N2.5-4	3000	21	66	3000	4.0	84.5
25.	R80-M20-Ah-N0.25-3	3000	21	57	3210	2.0	0
26.	R80-M20-Ah-N0.25-3	3000	25	91	3230	3.3	65.5
27.	R80-M20-Ba-N0.25-3	2960	23	65	3230	3.0	0
28.	R80-M20-Ba-N0.25-3	3000	24	90	3190	3.0	76
29.	R80-M20-Ba-N2.5-4	3000	21	45	2870	2.7	98
30.	R80-M20-Ba-N2.5-4	3000	20	60-90	3000	0.25	100
31.	R80-M20-Ba-N5-1	2975	25	28	2700	2.0	19*
32.	R80-M20-Ba-N5-1	2940	26	135	2830	0.1	100*
33.	R80-M20-T-As-1	3000	29	80	3200	2	62
34.	R80-M20-T-As-2	3000	27	110 (→156)	3600 (→4400 →3180)	0.05	100
35.	R80-M20-T-As-3	3000	21	46	3140	2.7	23
36.	R80-M20-T-As-3	3000	28	51	3000	5.0	55

TABLE 18--Continued

Batch No.	Catalyst Code Number	Conditions of Hydrogenation: Initial pres. psi	Initial temp. °C	Avg. temp. °C	Avg. pres. psi	Time hrs.	% θ Yield (Aniline)
37.	R80-M20-T-As-3	3000	21	65	2930	3.3	100
38.	R80-M20-T-As-3	3000	21	70	3120	1.33	92.5
39.	R80-M20-T-As-3	3000	25	110 (→219)	3440 (→3940 →2910)	0.08	100
40.	R68-M32-Ah-N6-1	2975	31	160	3110	2.0	95*(without agitation)
41.	R68-M32-Ah-N6-1	3025	29	103	2850	0.75	100*
42.	R50-M50-Ah-N5-2	3220	27	82	3645	2.0	29
43.	R50-M50-Ah-N5-2	3000	29	95	3210	0.84	100
44.	R50-M50-Ah-N5-2	3160	26	122	3600	0.75	100
45.	R50-M50-Ah-N2.5-4	3010	25	64	3170	4.0	31.5
46.	R50-M50-Ba-N2.5-4	3000	24	49	3080	2.0	58
47.	R50-M50-Ba-N2.5-4	3015	25	50	3050	2.7	84
48.	R50-M50-Ba-N5-1	3000	24	112	3300	1.0	100
49.	R50-M50-T-As-1	2980	29	92 (→192)	3300	0.3	100
50.	R50-M50-T-As-3	3000	27	72	3160	1.33	70
51.	R40-M60-Ah-N6-1	2875	31	105	3425	2.0	0*(without agitation)
52.	R40-M60-Ah-N6-1	3020	33	110	2900	2.0	100*
53.	R20-M80-Ah-N5-2	3160	22	127	3800	0.75	98
54.	R20-M80-Ah-N5-2	3000	29	130	3180	1.16	100
55.	R20-M80-Ah-N2.5-4	3000	23	66	3070	4.0	62

TABLE 18--Continued

Batch No.	Catalyst Code Number	Initial pres. psi	Initial temp. °C	Conditions of Hydrogenation Avg. temp. °C	Avg. pres. psi	Time hrs.	% ◈ Yield (Aniline)
56.	R20-M80-Ba-N2.5-4	3010	26	44	3040	2.7	0
57.	R20-M80-Ba-N2.5-4	3000	23	47	3220	2.5	0
58.	R20-M80-Ba-N5-1	3000	40	107	3500	2.0	13
59.	R20-M80-T-As-1	3020	27	140 (→214)	3610	0.25	97
60.	R20-M80-T-As-3	3000	27	74	3260	1.33	57.5
61.	R18-M82-Ah-N6-1	3000	31	105	3190	2.0	19* (without agitation)
62.	R18-M82-Ah-N6-1	2875	32	110	2700	1.0	100*

◈The % yield was determined by chemical extraction method.

*The hydrogenation was performed in Magne-dash apparatus. All other hydrogenations were performed in the amino autoclave.

#Only 0.1 mole of nitrobenzene in 10 ml. of ethanol was used.

TABLE 19

Hydrogenation of Nitrobenzene (0.2 mole) in Ethanol (20 ml.) with Rhenium Heptasulfide (Code Number R100-M0-Ah-N0.25-1) and Molybdenum Sulfide (Code Number R0-M100-Ah-N2.5-4) Mixed in Various Proportions as Catalysts (2.5 g. per mole of Substrate)

Batch No.	Catalyst Proportion of Re_2S_7 : MoS_3	Initial pres. psi	Initial temp. °C	Conditions of Hydrogenation Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield# (Aniline)
1.	100 : 0	3000	22	64	3200	4	38.0
2.	80 : 20	3000	23	67	2990	4	37.0
3.	52.4 : 47.6 ⇳	3000	26	64	3220	4	26.0
4.	29.3 : 70.7 ⇲	3000	25	64	3240	4	16.1
5.	20 : 80	3000	27	64	2740	4	6.9
6.	15 : 85	3000	26	68	3350	4	4.6*
7.	0 : 100	3000	25	74	3350	4	0*

#The percentage yield was determined by chemical extraction methods.

*The hydrogenation was performed in Magne-dash apparatus. All others were performed in the aminco apparatus.

⇳The mixed catalyst would have same rhenium and molybdenum contents as R50-M50-Ah-N2.5-4.

⇲The mixed catalyst would have the same rhenium and molybdenum contents as R20-M80-Ah-N2.5-4.

TABLE 20

Hydrogenation of Styrene (0.2 mole) in Ethanol (20 ml.) with Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts (2.5 g. per mole of Substrate)*

Batch No.	Catalyst Code Number	Conditions of Hydrogenation: Initial pres. psi	Initial temp. °C	Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield (Ethylbenzene, the rest are styrene and polystyrene)
1.	None	3000	22	123	3790	2.2	0
2.	R0-M100-Ah-N2.5-4	3000	23	124	3850	2.2	0
3.	R100-M0-Ah-N0.25-1	3000	25	110	3420	2.2	19.2
4.	R100-M0-Ba-N5-1	2970	27	113	3180	1.0	52
5.	R80-M20-Ah-N5-2	3000	25	120	3600	2.5	80.6
6.	R80-M20-Ah-N5-2	3000	27	134	3600	1.0	91
7.	R80-M20-Ah-N2.5-4	3000	27	114	3700	2.2	16
8.	R80-M20-Ah-N2.5-4	3000	24	122	3770	1.5	17
9.	R80-M20-Ah-N2.5-4	3000	27	137.5	3820	1.0	23.5
10.	R80-M20-Ba-N2.5-4	3000	24	97	3390	1.0	100
11.	R80-M20-Ba-N2.5-4	3000	25	138.5	3500	1.0	100
12.	R80-M20-Ba-N5-1	3000	18	130	3720	2.0	96.5
13.	R80-M20-T-As-1	3000	29	110	3590	2.0	48
14.	R80-M20-T-As-3	3000	24	114	3630	0.16	40
15.	R80-M20-T-As-3	3000	24	127	3645	1.0	82.5
16.	R50-M50-Ah-N5-2	3000	26	147	3920	0.25	14
17.	R50-M50-Ah-N5-2	3000	26	155	3750	1.0	32.5
18.	R50-M50-Ah-N2.5-4	3000	27	124	3760	2.2	15.5
19.	R50-M50-Ba-N2.5-4	3000	25	99	3540	1.0	34

TABLE 20--Continued

Batch No.	Catalyst Code Number	Initial pres. psi	Initial temp. °C	Conditions of Hydrogenation Avg. temp. °C	Avg. pres. psi	Time hrs	% Yield (Ethylbenzene, the rest are styrene and polystyrene)
20.	R50-M50-Ba-N5-1	3000	18	125	3850	2.0	48
21.	R50-M50-T-As-3	3085	31	125	3710	1.0	45
22.	R20-M80-Ah-N5-2	3000	27	147	3860	1.0	33
23.	R20-M80-Ah-N2.5-4	3000	27	124	3760	2.2	21.5
24.	R20-M80-Ba-N2.5-4	3000	27	99	3540	1.0	0
25.	R20-M80-Ba-N2.5-4	3000	27	124	3665	1.0	21
26.	R20-M80-Ba-N5-1	2970	21	112	3700	2.0	10
27.	R20-M80-Ba-N5-1	3000	23	129	3800	1.0	14.5
28.	R20-M80-T-As-1	2930	29	113	3515	2.0	29
29.	R20-M80-T-As-2	3000	29	131	3650	1.0	67.5
30.	R20-M80-T-As-3	3000	27	133	3750	1.0	68
31.	R20-M80-T-As-3	3110	37	140	3785	1.0	73.5

*All hydrogenations were performed in the Aminco autoclave.

TABLE 21

Hydrogenation of Cyclohexanone (0.2 mole) with mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts (2.5 g. per mole of Substrate)

Batch No.	Catalyst Code Number	Conditions of Hydrogenation: Initial pres. psi	Initial temp. °C	Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield (Cyclohexanol)
1.	None	3000	21	177	4090	3.0	0
2.	R0-M100-Ah-N2.5-4	3000	26	176	4240	3.0	22*
3.	R100-M0-Ah-N0.25-1	3000	22	174	4000	3.0	100
4.	R80-M20-Ah-N2.5-4	3000	27	183	4130	<3	100
5.	R80-M20-Ba-N2.5-4	3000	23	111	3615	1.0	92
6.	R80-M20-Ba-N2.5-4	3000	23	115	3650	1.33	100
7.	R80-M20-Ba-N5-1	2960	25	104	3530	2.0	27*
8.	R80-M20-Ba-N5-1	2775	23	150	3490	1.5	82*
9.	R80-M20-T-As-3	3000	23	148	3870	1.66	85
10.	R50-M50-Ah-N2.5-4	3000	23	175	4180	3.3	50
11.	R50-M50-Ba-N2.5-4	3000	22	110	3750	1.0	0
12.	R50-M50-Ba-N2.5-4	3000	23	150	3900	2.7	100
13.	R50-M50-Ba-N5-1	3000	25	164	4130	2.0	45
14.	R50-M50-T-As-3	3000	24	151	4010	1.66	23
15.	R20-M80-Ah-N2.5-4	3000	24	175	4030	3.0	62
16.	R20-M80-Ba-N2.5-4	3000	22	108	3760	1.0	0
17.	R20-M80-Ba-N2.5-4	3000	27	150	4000	2.7	22
18.	R20-M80-Ba-N5-1	2960	25	152	4000	2.0	0
19.	R20-M80-T-As-3	3000	26	153	4020	1.66	0

*The hydrogenation was performed in Magne-dash apparatus. All others were carried out in the Aminco apparatus.

IV. GENERAL DISCUSSION

A. Methods for the Analyses of Molybdenum Sulfide, Rhenium Sulfide, and Mixtures of the Sulfides.

1. Preparation of Solutions.

(a) Mixtures of concentrated sulfuric and nitric acids were effective in bringing the sulfides into solution. There was no loss of molybdenum. However, a serious loss of rhenium (up to 85%) was found when the solution was heated three times at its fuming point. In addition, since sulfuric acid was used as reagent, the sulfur content could not be determined simultaneously from the solution.

(b) In the case of using sodium peroxide, potassium perchlorate and sucrose as the oxidizing reagents, the fusion was not successful since a residue as high as 9% was found. The perchlorate ion would interfere the precipitation of rhenium with tetraphenylarsonium chloride; therefore, the rhenium content could not be determined from the solution. Also, a considerable amount of precipitate of unknown composition was found when the solution was neutralized with acid in the determination of either molybdenum or sulfur. There, of course, resulted a serious loss of molybdenum and sulfur.

(c) In using aqua regia and bromine as reagents, the determination of both sulfur and molybdenum seemed to be satisfactory. However, about a 30% loss of rhenium was found when the solution was evaporated twice to dryness in order to remove

the nitric acid.

(d) The procedure for the preparation of solutions of the sulfides with 30% H_2O_2 in alkaline solution was found to be the most convenient one out of the four oxidizing reagents recommended. All the data obtained for the determination of rhenium, molybdenum, and sulfur seemed to be correct. The hydrogen peroxide was found to be a little less effective in bringing the sulfides into solution from a 5N NH_4OH solution than from a 5N NaOH solution (refer to Table 12, p. 64). However, the residue was only less than 0.5% of the sample when it was carried in the ammonium hydroxide solution. Also, it was found to be more convenient for the subsequent determination of rhenium by the tetraphenylarsonium perrhenate method in 6M ammonium hydroxide solution if 5N NH_4OH had been used for the preparation of solution.

2. Tetraphenylarsonium Perrhenate Method for the Determination of Rhenium.

(a) The rhenium content of pure rhenium sulfide may be determined by this method in solutions varying from strongly ammonical (6M) to moderately acidic (5M HCl). From Table 6 (p. 51), the precipitation of rhenium from 6M NH_4OH solution was shown to be more satisfactory than that from 6M HCl solution.

(b) In mixtures of rhenium and molybdenum sulfides, molybdenum would coprecipitate with rhenium if the precipitation was carried in 5M HCl solution. The precipitation of rhenium from either a solution of 6M NH_4OH or of 0.6M tartaric

acid seemed to depend on the relative quantity of the molybdenum present. If rhenium and molybdenum were present in equal or nearly so proportion, molybdenum would not interfere. If the relative quantity of molybdenum was much higher, a positive error would be the result due to the contamination of molybdenum. If the relative quantity of molybdenum was much lower, a negative error would be the usual one. The effects mentioned seemed to be more predominant in case of 0.6M tartaric acid solution than 6M ammonium hydroxide solution (refer to Table 7, p. 53).

3. Permanganate Titration Method for the Determination of Molybdenum and Rhenium.

(a) In the determination of molybdenum in pure molybdenum sulfide, this method gave a pretty accurate result with a very convenient procedure, especially in routine work.

(b) In the determination of rhenium in pure rhenium sulfide, only small amounts, less than 30 mg., can be handled (refer to Table 9, p. 56).

(c) In presence of molybdenum, the determination of rhenium by this method was found to be not satisfactory even when molybdenum had been previously precipitated by ∝-benzoinoxime (refer to Table 9, p. 56).

(d) In the same way, in presence of rhenium, the determination of molybdenum was not practical even when the rhenium had been previously precipitated by tetraphenylarsonium chloride.

4. ∝-Benzoinoxime Method and Lead Molybdate Method for the Determination of Molybdenum.

(a) Both methods were found to be equally accurate for the determination of molybdenum in a solution containing either pure molybdenum or mixture of molybdenum and rhenium in any proportions (refer to Table 11, p. 63, and Table 13, p. 66).

(b) If the appropriate amount of molybdenum content in a sample to be analyzed is known, the ∝-benzoinoxime method is more convenient to manipulate; otherwise the lead molybdate method is preferred.

B. The Preparation of Catalysts.

1. The Drying of Catalysts.

(a) In the drying of catalysts in a vacuum pistol over P_2O_5 under a high vacuum of 50-100 microns with bromobenzene (b.p., 156.4°C) as the heating medium, the catalyst was first fairly dried at room temperature in a desiccator packed with anhydrous $CaCl_2$ or other suitable drying reagents under a moderate vacuum of few millimeters. Otherwise, the rapid release of the moisture from the catalyst blew away some of the catalyst and sometimes caused a serious loss of product. Even though the catalyst had been fairly dried at room temperature before transferring to the vacuum pistol, it was still advisable to dry the catalyst in the vacuum pistol under high vacuum first at a temperature of 40-60°C for 2-3 hours, and then at the boiling point of bromobenzene, i.e., 156°C, to constant weight.

(b) In the drying of catalysts in a vacuum oven over

P_2O_5 under high vacuum, it was found that the temperature should be kept below 100°C, otherwise the phosphorus pentoxide in the oven would sublime and contaminate the catalysts. The catalysts of code numbers R80-M20-Ah-NO.25-3 and R80-M20-Ba-NO.25-3 were contaminated with sublimed P_2O_5 when they were dried in the vacuum oven at a temperature of 150°C. At temperatures above 100°C, other drying reagents such as concentrated sulfuric acid, "anhydrone," and "molecular sieve" might fit the job.

(c) Since both rhenium heptasulfide and molybdenum sulfide will decompose and lose their sulfur through sublimation when they are heated at moderately high temperature at atmospheric pressure, some of the catalysts prepared showed such serious losses as they were heated in the vacuum pistol with diphenylether (b.p., 258.3°C) as the heating medium. Meanwhile the pistol gradually lost its vacuum due to leakage.

(d) It seemed difficult to get rid of all the moisture content from the catalyst. The catalysts still contained a few per cent of moisture after they had been dried to constant weight in a vacuum pistol over P_2O_5 under 50-100 microns with bromobenzene as the heating medium for more than 100 hours.

2. The Precipitation of Molybdenum Sulfide by Hydrogen Sulfide.

(a) The precipitation of molybdenum sulfide by H_2S from a hydrochloric acid solution of molybdate was usually incomplete, and the more incomplete from the acid of higher concentrations. The precipitation seemed easier in sulfuric

acid solution than in hydrochloric acid solution of the same concentration. Incomplete precipitation was caused by a reduction of part of the molybdenum by hydrogen sulfide. The reduced compound was then only very slowly precipitated even in a pressure bottle. Most of the molybdenum sulfides prepared were thus found to be of a composition of $xMoS_3.yMoS_2$.

(b) Since molybdenum sulfides are soluble in alkaline sulfide, the precipitation of molybdenum sulfide by H_2S from an ammonium hydroxide solution was followed by acidification with hydrochloric or sulfuric acid.

3. The Precipitation of Rhenium Heptasulfide by Hydrogen Sulfide.

(a) The precipitation of rhenium heptasulfide by H_2S from a hydrochloric acid solution of perrhenate required prolonged treatment and was more satisfactory at high concentrations of acid. The precipitation from more dilute acids was incomplete probably unless performed in hot solutions under pressure.

(b) The precipitation of rhenium heptasulfide by H_2S from an ammonium hydroxide solution of perrhenate is slow and only becomes complete when the solution is further acidified with hydrochloric or sulfuric acid.

4. The Co-precipitation of Mixtures of Rhenium and Molybdenum Sulfides by Hydrogen Sulfide.

(a) The co-precipitation of mixtures of rhenium and molybdenum sulfides of various compositions by H_2S from either hydrochloric acid or ammonium hydroxide solutions of perrhenate

and molybdate seemed to be subject to the principles mentioned in the foregoing paragraphs (3) and (4).

(b) The co-precipitation of mixtures of rhenium and molybdenum sulfides of various compositions by H_2S could be accomplished nearly completely by first saturating an ammonium hydroxide solution of moderate concentration (greater than 2.5N) of perrhenate and molybdate with the gas followed by acidification with hydrochloric or sulfuric acid to fairly acidic conditions and then allowing to stand for several hours preferably overnight.

5. The Precipitation of Molybdenum Sulfide, Rhenium Heptasulfide, and Mixtures of the Sulfides by the Treatment of Sulfuric Acid Solutions of the Corresponding Salts with Thiosulfate.

(a) From Table 22, the completeness of the precipitation of the sulfides by the treatment of sulfuric acid solutions of the corresponding salts with thiosulfate followed by the extraction of free sulfur with toluene seemed to be nearly same as that by the saturation of the sulfuric acid solutions with H_2S.

(b) The catalysts usually contained considerable amounts of free sulfur which could be extracted with a suitable solvent in a Soxhlet extraction apparatus. Toluene was preferable to CS_2 as the extraction solvent. However, 20-24 hours was found to be the optimum time interval for the extraction of the free sulfur contained in the catalysts. In case of prolonged extraction, molybdenum and even rhenium, as well

TABLE 22

A Comparison of the Percentage of Yield of the Precipitation of Sulfides from Sulfuric Acid Solutions of Corresponding Salts by Thiosulfate with That by Hydrogen Sulfide

Type of Catalyst	Catalyst Code Number	Concentration of H_2SO_4 Solution	Reagent	% Yield (on dry basis)
MoS_3	RO-M100-As-NO.5-1	1.35 - 0.5N	H_2S	69.5
MoS_3	RO-M100-T-As-3	1.6N	$Na_2S_2O_3$	53.0
Re_2S_7	R100-MO-T-As-3	1.0N	"	70.5
Re_2S_7	R100-MO-T-As-4	0.85N	"	64.7
$Re_2S_7.MoS_3$	R80-M20-T-As-3	1.6N	"	77.1
$Re_2S_7.MoS_3$	R50-M50-T-As-3	1.6N	"	72.8
$Re_2S_7.MoS_3$	R20-M80-T-As-3	1.6N	"	65.0

as the combined sulfur, were found to be extracted by toluene, as indicated in Table 23.

TABLE 23

Extraction of the Catalysts with Toluene

Catalyst Code Number	Time for Extraction hours	% Yield (on dry basis)	Composition of the Catalyst (on dry basis) % Rhenium	Molybdenum	Sulfur
RO-M100-T-As-2	168	40.3	-	27.4	74.6
RO-M100-T-As-3	24	50.0	-	36.8	63.2
R100-MO-T-As-3	24	70.5	67.9	-	32.1
R100-MO-T-As-4	24	64.7	61.8	-	38.2
R80-M20-T-As-1	504	61.1	60.5	7.6	31.9
R80-M20-T-As-3	24	77.1	49.1	10.0	40.9
R50-M50-T-As-1	504	27.1	54.7	13.8	31.5
R50-M50-T-As-3	24	72.8	35.7	23.6	40.7
R20-M80-T-As-1	168	37.7	29.6	43.4	27.0
R20-M80-T-As-3	24	65.0	15.4	44.6	40.0

C. Catalytic Hydrogenation.

1. Chemical Nature of Substrates.

The ease with which substrates undergo catalytic hydrogenations depends upon their chemical natures. Nitrobenzene

was found to undergo catalytic hydrogenations much easier than styrene, which in turn was somewhat easier than cyclohexanone, as shown from the data summarized in Table 24. In general this means that the nitro group is much more active in reaction with hydrogen gas than the carbon to carbon double bond conjugated with a benzene ring, and the latter in turn is more active than the carbon to oxygen double bond.

TABLE 24

A Comparison of Catalytic Hydrogenations of Nitrobenzene, Styrene, and Cyclohexanone with Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts

Catalyst Code Number	Substrate	Conditions of Hydrogenation* Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield	References Table No.	Batch No.
R80-M20-Ba-N2.5-4	$PhNO_2$	60-90	3000	0.25	100	18	30
"	$PhCH=CH_2$	97	3390	1.0	100	20	10
"	Cy=O	115	3650	1.33	100	21	6
R80-M20-Ba-N5-1	$PhNO_2$	135	2830	<0.1	100	18	32
"	$PhCH=CH_2$	130	3720	2.0	96.5	20	12
"	Cy=O	150	3490	1.5	82	21	8
R80-M20-T-As-3	$PhNO_2$	70	3120	1.33	92.5	28	38
"	$PhCH=CH_2$	127	3645	1.0	82.5	20	15
"	Cy=O	148	3870	1.66	85.0	21	9
R50-M50-Ba-N2.5-4	$PhNO_2$	49	3080	2.0	58	18	46
"	$PhCH=CH_2$	99	3540	1.0	34	20	19
"	Cy=O	100	3750	1.0	0	21	11

TABLE 24--Continued

Catalyst Code Number	Substrate	Conditions of Hydrogenation* Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield	References Table No.	Batch No.
R50-M50-Ba-N5-1	$PhNO_2$	112	3300	1.0	100	18	48
"	$PhCH=CH_2$	125	3850	2.0	48	20	20
"	Cy=O	164	4130	2.0	45	21	13
R50-M50-T-As-3	$PhNO_2$	75	2755	1.33	99	18	50
"	$PhCH=CH_2$	125	3710	1.0	45	20	21
"	Cy=O	151	4010	1.66	23	21	14
R20-M80-Ba-N5-1	$PhNO_2$	107	3500	2.0	13	18	58
"	$PhCH=CH_2$	112	3700	2.0	10	20	16
"	Cy=O	152	4000	2.0	0	21	18
R20-M80-T-As-3	$PhNO_2$	74	3260	1.33	57.5	18	60
"	$PhCH=CH_2$	133	3750	1.0	68	20	30
"	Cy=O	153	4020	1.66	0	21	19

*All were carried out under an initial pressure of about 3000 psi.

2. Influence of Temperature.

Temperature is an important factor in the hydrogenation reactions. In Table 25, some data are tabulated as examples to show the influence of temperature in catalytic hydrogenations of nitrobenzene, styrene, and cyclohexanone.

TABLE 25

Influence of Temperature in the Catalytic Hydrogenations of Nitrobenzene, Styrene, and Cyclohexanone with Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts

Catalyst Code Number	Substrate	Conditions of Hydrogenation* Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield	References Table No.	Batch No.
RO-M100-T-As-3	$PhNO_2$	107	3700	12	14	18	12
"	"	150-175	3860	12	94.5	"	13
R80-M20-Ah-N2.5-4	"	55	2990	5	61	"	22
"	"	66	3000	4	84.5	"	24
R80-M20-Ba-NO.25-3	"	65	3230	3	0	"	27
"	"	90	3190	3	76	"	28
R80-M20-T-As-3	"	46	3140	2.7	23	"	35
"	"	70	3120	1.33	92.5	"	38
"	"	110 (→219)	3440 (→3940 →2910)	0.08	100	"	39
R50-M50-Ah-N5-2	"	82	3645	2.0	29	"	42
"	"	95	3210	0.84	100	"	43
"	"	122	3600	0.75	100	"	44
R80-M20-Ah-N5-2	$PhCH=Ch_2$	120	3600	2.5	80.6	20	5
"	"	134	3600	1.0	91	"	6
R80-M20-Ah-N2.5-4	"	114	3700	2.2	16	"	7
"	"	122	3770	1.5	17	"	8
"	"	137.5	3820	1.0	23.5	"	9

TABLE 25--Continued

Catalyst Code Number	Substrate	Conditions of Hydrogenation* Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield	References Table No.	Batch No.
R20-M80-Ba-N2.5-4	$PhCH=Ch_2$	99	3540	1	0	20	24
"	"	124	3665	1	21	"	25
R20-M80-Ba-N5-1	"	112	3700	2	10	"	26
"	"	129	3800	1	14.5	"	27
R20-M80-T-As-3	"	133	3750	1	68	"	30
"	"	140	3785	1	73.5	"	31
R80-M20-Ba-N5-1	Cy=0	104	3530	2.0	27	21	7
"	"	150	3490	1.5	82	"	8
R50-M50-Ba-N2.5-4	"	110	3750	1.0	0	"	11
"	"	150	3900	2.7	100	"	12
R20-M80-Ba-N2.5-4	"	108	3760	1.0	0	"	16
"	"	150	4000	2.7	22	"	17

*All were carried out under an initial pressure of about 3000 psi.

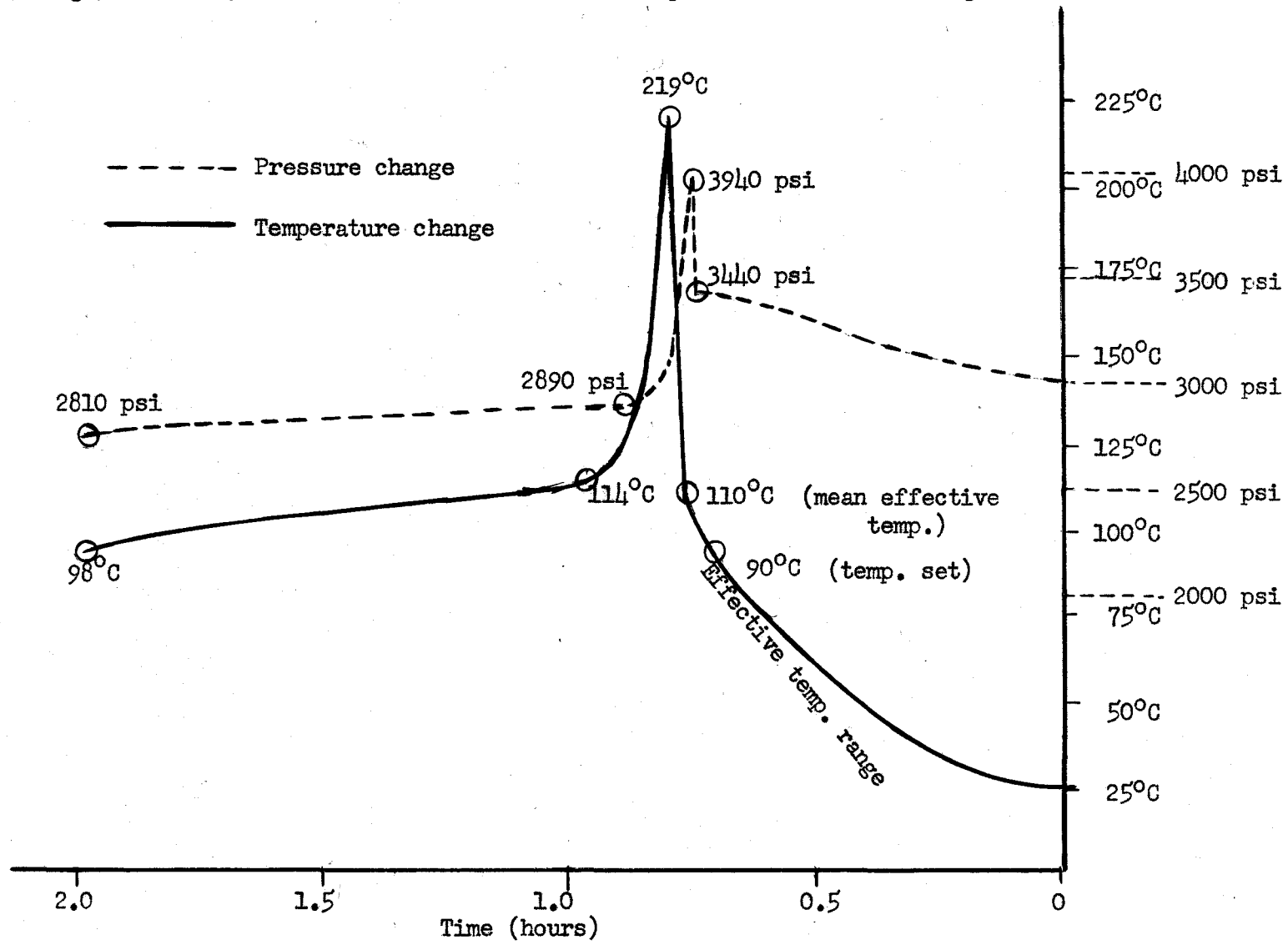
3. Heat of Hydrogenation and Mean Effective Temperature.

In the experiments, it was found that even though the hydrogenation apparatus with the contents was heated to a certain desired temperature and an effort was made to keep that temperature by means of a voltage regulator, the actual working

temperature always showed some variation. This was because of the heat of hydrogenation of the substrates and the catalytic activity of the catalysts used. In the case of hydrogenation of such a substrate which has a large value of heat of hydrogenation as nitrobenzene (its ΔH was calculated as -132 Kcal per mole at 25°C) with a relative active catalyst, it was found difficult to keep the working temperature at the desired point. The hydrogenation of nitrobenzene with the catalyst of code number R80-M20-T-As-3 (Batch No. 39, Table 18) shown in Fig. 7 was a typical illustration.

In this experiment, the Aminco autoclave was charged to 3000 psi at 25°C and gradually heated to the desired temperature of 90°C. However, 90°C was already in the effective temperature range of nitrobenzene with R80-M20-T-As-3 as catalyst; the temperature could not be kept (even the electrical heating device had been turned off) from further rising due to the heat evolved in the reaction. Finally a mean effective temperature, 110°C in this case, was attained; the hydrogenation went at its maximum velocity accompanied with an abrupt temperature rise (from 110°C to 219°C) and a steep pressure drop (from 3940 psi to 2890 psi). It was complete in less than five minutes. Those hydrogenations of nitrobenzene listed in Table 18, of Batch Nos. 15, 20, 32, 34, 41, 43, 44, 49, and 59, showed nearly the same situations. Therefore, it would be advisable to keep at a minimal temperature, especially in the hydrogenation of those substrates which have large values of heat of reaction. Otherwise a big error might be made if the readings

Fig. 7.--Hydrogenation of Nitrobenzene (0.2 mole) in Ethanol (20 ml.) with R80-M20-T-As-3 (0.5 g.) as Catalyst in Aminco Autoclave (Time-Temperature-Pressure Changes).



of temperature and pressure changes were taken at interval times of thirty minutes or so in the case that the hydrogenation apparatus was not equipped with a self-recording machine.

4. Influence of Pressure.

The pressure of hydrogen as well as temperature plays an important role in the hydrogenation reactions. For an example, in the hydrogenation of nitrobenzene using pure molybdenum sulfide as catalyst it was found that there was no aniline produced if the reaction was carried under an average pressure of 2300 psi at an average temperature of 120°C for 2.5 hours.[5] However, it was found by the writer in several experiments that there was aniline produced if the reactions were carried under an average pressure higher than 3250 psi even at a temperature of few degrees lower than 120°C and in less than 2.5 hours. The data are tabulated in Table 26.

TABLE 26

Influence of the Pressure of Hydrogen in the Hydrogenations of Nitrobenzene (0.2 mole) in Ethanol (20 ml.) with Pure Molybdenum Sulfide as Catalysts

Catalyst Code Number	Conditions of Hydrogenation: Avg. pres. psi	Avg. temp. °C	Time hrs.	% Yield (Aniline)	References	
RO-M100-Ah-NO.3-x*	2300	120	2.5	0	5	
RO-M100-Ah-NO.25-1	3450	156	11	100	Table 18	Batch 3
RO-M100-Ba-NO.25-1	3330	114	2	5	"	6
RO-M100-Ba-N2.5-1	3270	117	3.5	47	"	8
RO-M100-Ba-N5-1	2990	105	3.5	17	"	10

*The code number was assigned in accordance with the assignment of those of other catalysts heretofore described.

In the hydrogenation reactions, the actual working pressure changed with the temperature and the degree of completeness of hydrogenation of substrate. However, an initial pressure of about 3000 psi was set for almost all the experiments herein recorded.

5. Influence of Mixing.

In the hydrogenations of nitrobenzene with mixtures of rhenium and molybdenum sulfides as catalysts, agitation, as expected, greatly affected the velocity of reactions, as shown in Table 27.

TABLE 27

Influence of Agitation in the Hydrogenations of Nitrobenzene (0.2 mole) in Ethanol (20 ml.) with Mixtures of Rhenium and Molybdenum Sulfides as Catalysts (2.5 g. per mole of Substrate)#

Catalyst Code Number	Conditions of Hydrogenation Avg. temp. °C	Avg. pres.* psi	Time hrs.	Agitation Cycles per minute	% Yield (Aniline)	References Table No.	Batch No.
R100-M0-Ah-N5-1	160	3100	6	0	100	18	14
"	120	2650	0.35	35-40	100	"	15
R68-M32-Ah-N6-1	160	3110	2.0	0	95	"	40
"	103	2850	0.75	35-40	100	"	41
R40-M60-Ah-N6-1	105	3425	2	0	0	"	51
"	110	2900	2	35-40	100	"	52
R18-M82-Ah-N6-1	105	3190	2	0	19	"	61
"	110	2700	1	35-40	100	"	62

#The hydrogenations were all performed in Magne-dash apparatus.

*All experiments were carried out under an initial pressure of about 3000 psi.

6. Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide in Hydrochloric Acid Solutions.

(a) In the hydrogenations of nitrobenzene.

From the data summarized in Table 28, the mixtures of the sulfides prepared from either 2.5N or 6N hydrochloric acid solutions showed promoter action. A curve with the rhenium contents of the mixtures prepared from 2.5N hydrochloric acid solutions as abscissas versus their respective % yields of hydrogenations under nearly same conditions as ordinate was drawn in Fig. 8. Actually, the curve would have some variations; however, it indicated the promoter action (co-activation) of the catalysts.

(b) In the hydrogenations of styrene.

From the data in Table 29, a curve with the rhenium contents of the mixtures as abscissas versus their respective % yields of hydrogenations as ordinates was drawn in Fig. 9. The catalysts also showed a promoter action (simple activation) in the hydrogenations of styrene.

(c) In the hydrogenations of cyclohexanone.

From the data in Table 30, a curve with the corresponding coordinates as in Figs. 8 and 9 was drawn in Fig. 10. The catalysts also showed a promoter action (simple activation) in the hydrogenations of cyclohexanone.

TABLE 28

Catalytic Hydrogenations of Nitrobenzene (0.2 mole) in Ethanol (20 ml.) with Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts (2.5 g. per mole of Substrate) Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide in Hydrochloric Acid Solutions

Catalyst Code Number	Compositions, % Re	Mo	S	Conditions of Hydrogenation Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield (Aniline)	References Table No.	Batch No.
R100-M0-Ah-N0.25-1*	63.8	0	36.2	64	3200	4	38	15 18	3 16
R80-M20-Ah-N2.5-4	54.5	7.5	38.0	66	3000	4	84.5	17 18	2 24
R50-M50-Ah-N2.5-4	35.4	22.9	41.7	64	3170	4	31.5	17 18	10 45
R20-M80-Ah-N2.5-4	19.8	33.9	46.3	66	3070	4	62	17 18	16 55
R0-M100-Ah-N2.5-4	0	50.3	49.7	74	3350	4	0	14 18	5 2
R40-M60-Ah-N6-1	24.9	34.0	41.1	105	3425	2	0#	17 18	23 51
R18-M82-Ah-N6-1	12.2	39.0	48.8	105	3190	2	19#	17 18	24 52
R40-M60-Ah-N6-1	24.9	34.0	41.1	110	2900	2	100	17 18	23 61
R18-M82-Ah-N6-1	12.2	39.0	48.8	110	2700	1	100	17 18	24 62

#The hydrogenation was performed without agitation.

*The catalytic activity might be somewhat less than those catalysts of same compositions but prepared in 2.5N hydrochloric acid solutions.

Fig. 8.--Catalytic Activities of Mixtures of Rhenium and Molybdenum of Various Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfides in 2.5 N Hydrochloric Acid Solutions in Hydrogenations of Nitrobenzene.

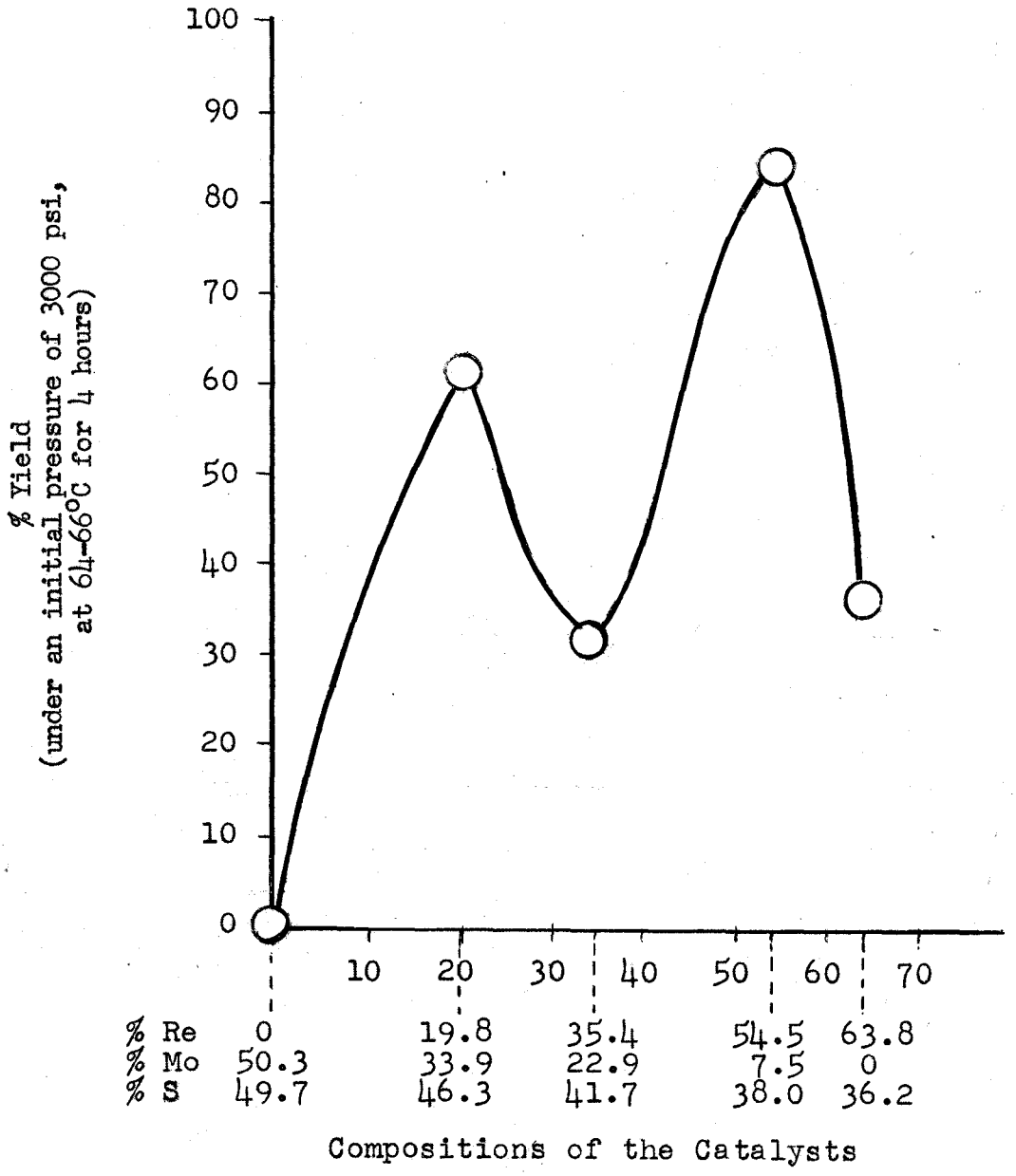


TABLE 29

Catalytic Hydrogenations of Styrene (0.2 mole) in Ethanol (20 ml.) with Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts (2.5 g. per mole of Substrate) Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfides in Hydrochloric Acid Solutions

Catalyst Code Number	Compositions Re	Mo (%)	S	Conditions of Hydrogenation Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield (PhC_2H_5)	References Table No.	Batch No.
R100-M0-Ah-N0.25-1*	63.8	0	36.2	110	3420	2.2	19.2 (30% at 124°C)#	15 20	3 3
R80-M20-Ah-N2.5-4	54.5	7.5	38.0	114	3700	2.2	16 (25% at 124°C)#	17 20	2 7
R50-M50-Ah-N2.5-4	35.4	22.9	41.7	124	3760	2.2	15.5	17 20	10 18
R20-M80-Ah-N2.5-4	19.8	33.9	46.3	124	3760	2.2	21.5	17 20	16 23
R0-M100-Ah-N2.5-4	0	50.3	49.7	124	3850	2.2	0	14 20	5 2

#The figures in the parentheses were deduced from the respective experimental data by extrapolation in order to plot a curve and, therefore, are only approximate.

*The catalytic activity might be somewhat less than those catalysts of same compositions but prepared in 2.5N hydrochloric acid solutions.

Fig. 9.--Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide in 2.5N Hydrochloric Acid Solutions in Hydrogenations of Styrene.

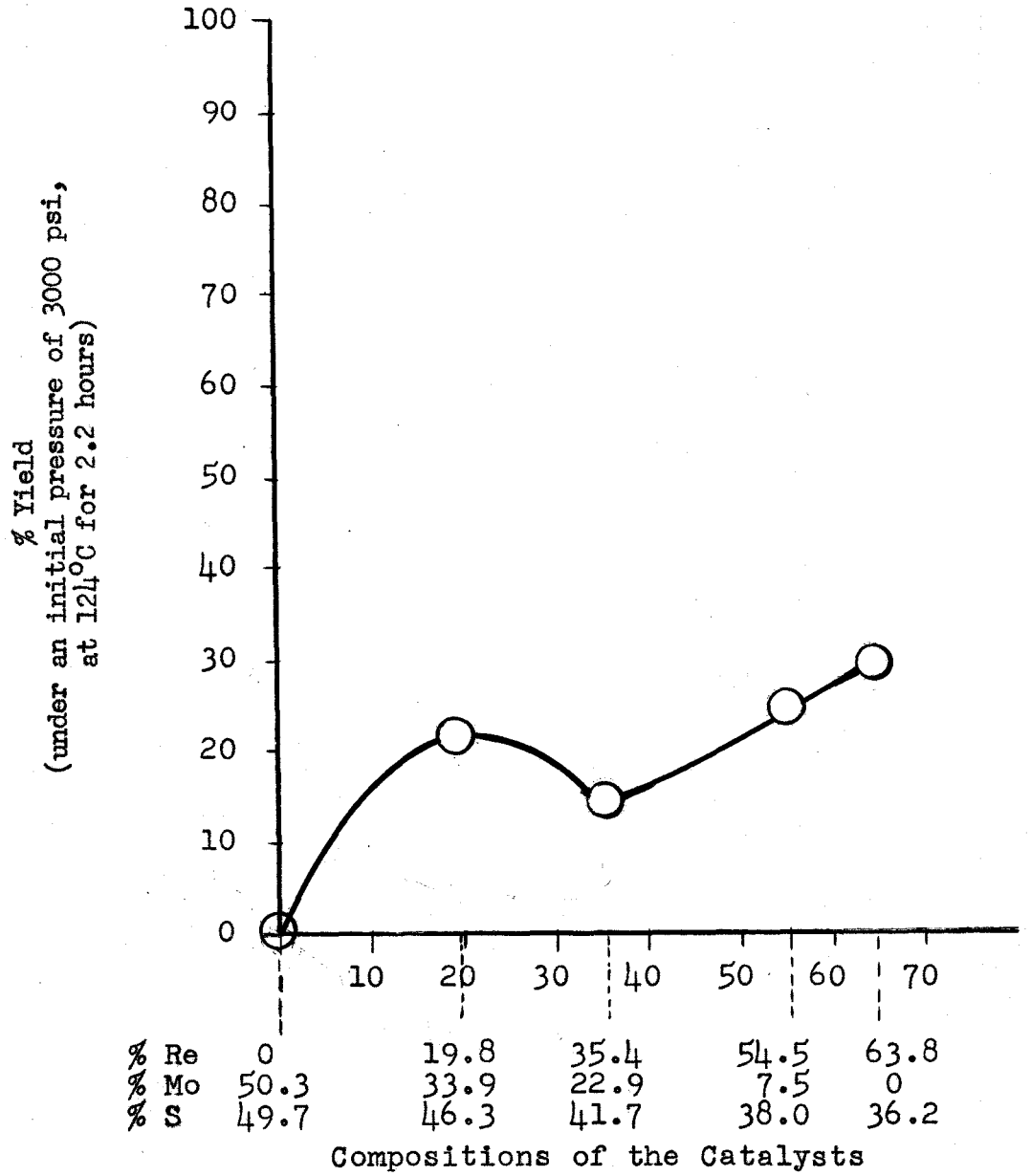


TABLE 30

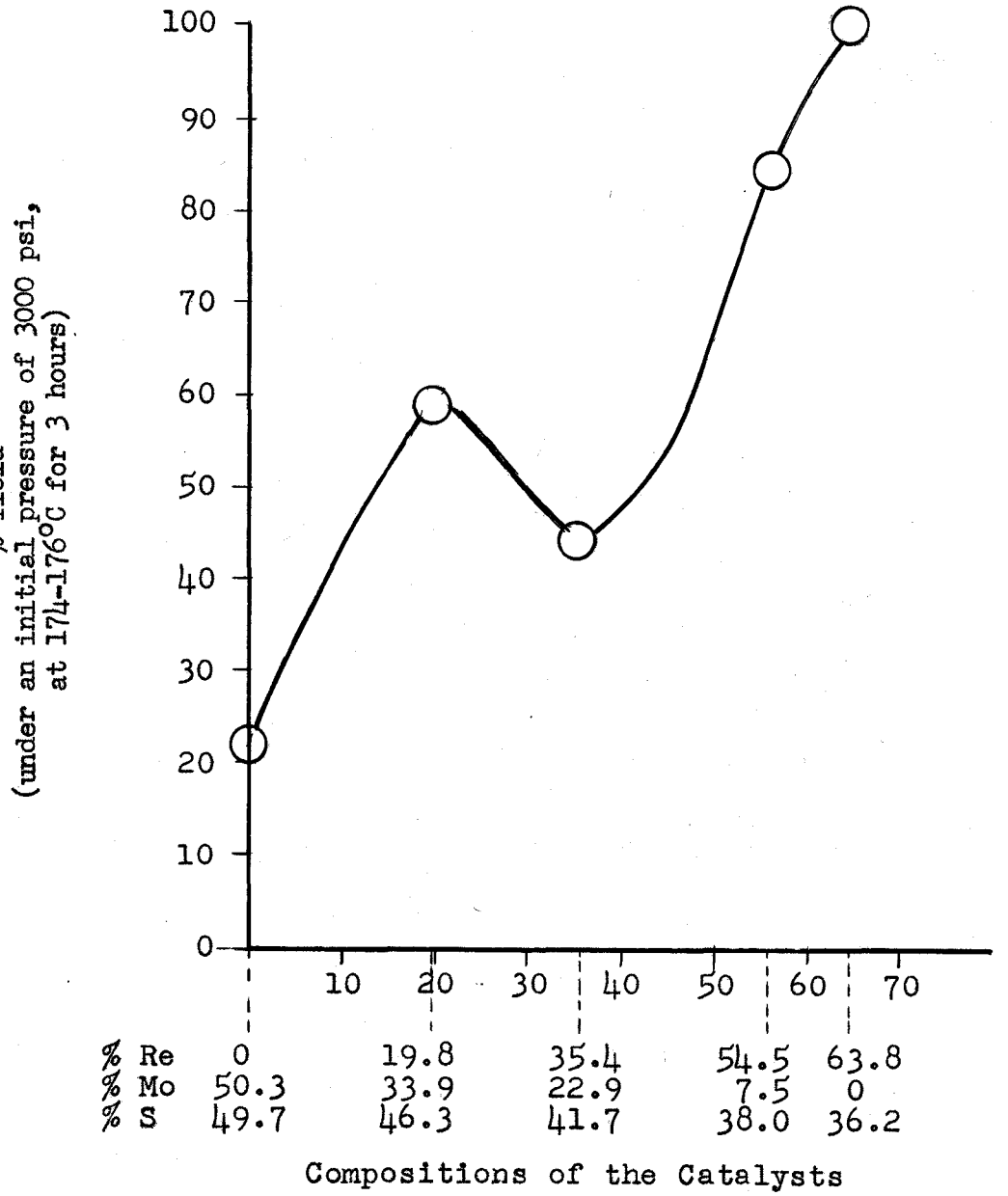
Catalytic Hydrogenations of Cyclohexanone (0.2 mole) with Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts (2.5 g. per mole of Substrate) Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide in Hydrochloric Acid Solutions

Catalyst Code Number	Compositions Re	Mo (%)	S	Conditions of Hydrogenation Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield (CyOH)	References Table No.	Batch No.
R100-M0-Ah-N0.25-1*	63.8	0	36.2	174	4000	3	100	15 21	3 3
R80-M20-Ah-N2.5-4	54.5	7.5	38.0	183	4130	3	100 (85% at 175°C)#	17 21	2 4
R50-M50-Ah-N2.5-4	35.4	22.9	41.7	175	4180	3.3	50 (45% for 3 hrs.)#	17 21	10 10
R20-M80-Ah-N2.5-4	19.8	33.9	46.3	175	4030	3	62	17 21	16 15
R0-M100-Ah-N2.5-4	0	50.3	49.7	176	4240	3	22	14 21	5 2

#The figures in the parentheses were deduced from the respective experimental data by extrapolation in order to plot a curve and, therefore, are only approximate.

*The catalytic activity might be somewhat less than those catalysts of same compositions but prepared in 2.5N hydrochloric acid solutions.

Fig. 10--Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide in 2.5N Hydrochloric Acid Solutions in Hydrogenations of Cyclohexanone.



7. Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide in Ammonium Hydroxide Solutions Followed by Acidification.

(a) Data on hydrogenation of nitrobenzene are listed in Table 31.

A curve for the catalysts prepared from 2.5N ammonium hydroxide solutions as listed in Table 31 was drawn in Fig. 11; however, the catalysts did not show any promoter action in the hydrogenations of nitrobenzene.

(b) Data on the hydrogenation of styrene using these catalysts are listed in Table 32.

A curve for the catalysts prepared from 5N ammonium hydroxide solutions as listed in Table 32 was drawn in Fig. 12; however, the catalysts did not show any promoter action in the hydrogenation of styrene.

(c) Data on the hydrogenation of cyclohexanone using these catalysts are listed in Table 33.

A curve for the catalysts prepared from 5N ammonium hydroxide solutions as listed in Table 33 was drawn in Fig. 13. However, the catalysts did not show any promoter action in the hydrogenations of cyclohexanone.

TABLE 31

Catalytic Hydrogenations of Nitrobenzene (0.2 mole) in Ethanol (20 ml.) with Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts (2.5 g. per mole of Substrate) Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide in Ammonium Hydroxide Solutions Followed by Acidification

Catalyst Code Number	Compositions Re	Mo (%)	S	Conditions of Hydrogenation Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield	References Table No.	Batch No.
R100-M0-Ba-N0.25-1*	62.3	0	37.7	50	2850	2.7	100	15 18	4 17
R80-M20-Ba-N2.5-4	45.3	8.8	45.9	45	2870	2.7	98	17 18	5 29
R50-M50-Ba-N2.5-4	30.8	23.3	45.9	50	3050	2.7	84	17 18	11 47
R20-M80-Ba-N2.5-4	13.0	37.8	49.2	44	3040	2.7	0	17 18	17 56
R0-M100-Ba-N2.5-4	0	47.2	52.8	59	3200	2.7	0	14 18	15 9
R50-M50-Ba-N5-1	31.1	25.8	43.1	112	3300	1	100	17 18	12 48
R20-M80-Ba-N5-1	13.0	37.6	49.4	107	3500	2	13	17 18	18 58
R0-M100-Ba-N5-1	0	47.4	52.6	105	3270	3.5	17	14 18	16 10

*The catalyst might have a higher catalytic activity than the one prepared in 2.5N ammonium hydroxide solution.

Fig. 11.--Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide in 2.5N Ammonium Hydroxide Solutions Followed by Acidification in Hydrogenations of Nitrobenzene.

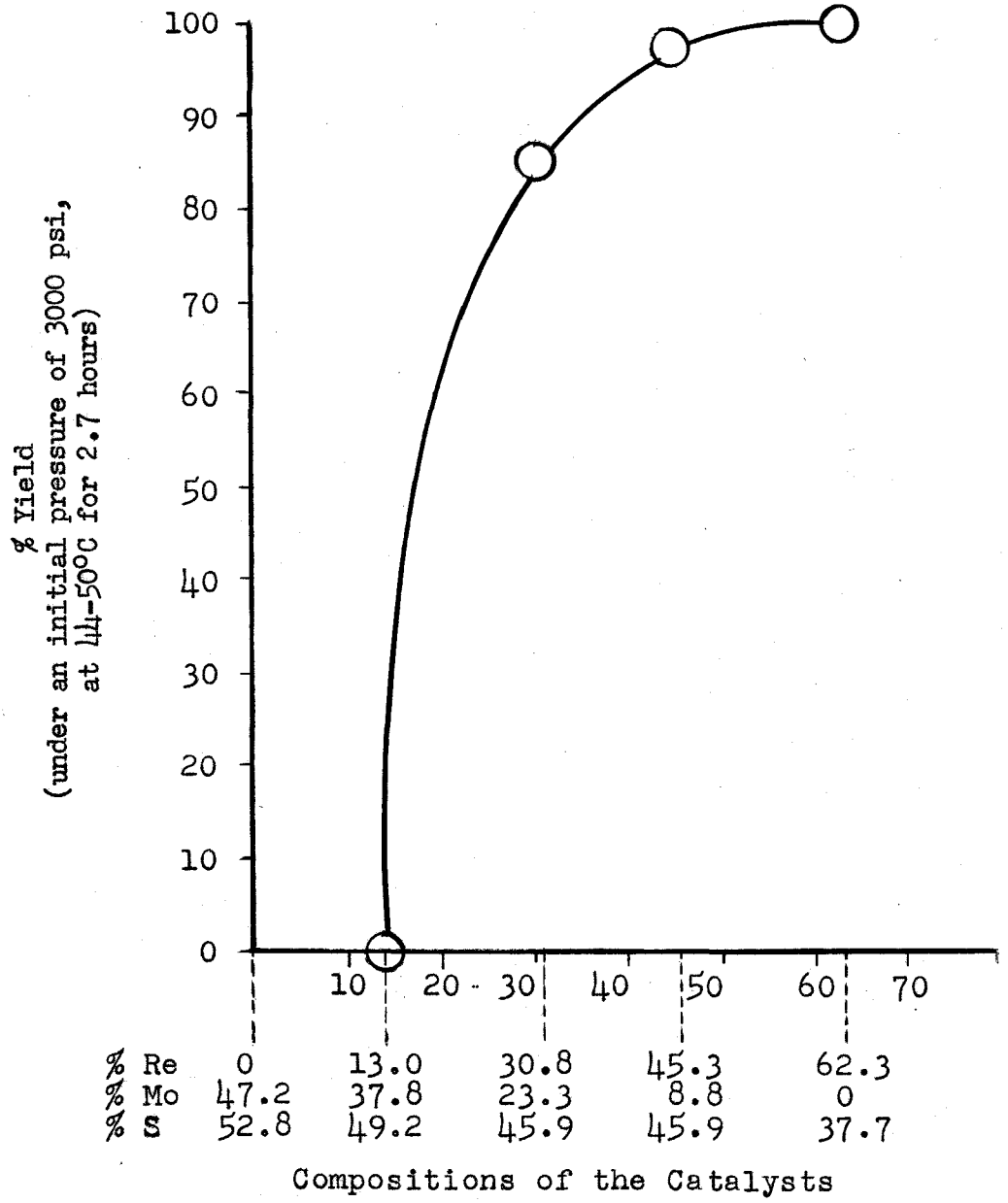


TABLE 32

Catalytic Hydrogenations of Styrene (0.2 mole) in Ethanol (20 ml.) with Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts (2.5 g. per mole of Substrate) Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide in Ammonium Hydroxide Solutions Followed by Acidification

Catalyst				Conditions of Hydrogenation				References	
	Compositions			Avg.	Avg.				
Code Number	Re	Mo (%)	S	temp. °C	pres. psi	Time hrs.	% Yield	Table No.	Batch No.
R80-M20-Ba-N2.5-4	45.3	8.8	45.9	97	3390	1	100	17 20	5 10
R50-M50-Ba-N2.5-4	30.8	23.3	45.9	99	3540	1	34	17 20	11 19
R20-M80-Ba-N2.5-4	13.0	37.8	49.2	99	3540	1	0	17 20	17 24
R100-M0-Ba-N5-1	71.0	0	29.0	113	3180	1	52 (>100% for 2 hrs.)#	15 20	5 4
R80-M20-Ba-N5-1	50.7	9.3	40.0	130	3720	2	96.5	17 20	6 12
R50-M50-Ba-N5-1	31.1	25.8	43.1	125	3850	2	48	17 20	12 20
R20-M80-Ba-N5-1	13.0	37.6	49.4	129	3800	1	14.5 (29% for 2 hrs.)#	17 20	18 27
R0-M100-Ba-N5-1	0	47.4	52.6	129	-	2	(0)#	14	16

#The figures were deduced from the relative, experimental data by extrapolation and, therefore, are only approximate.

Fig. 12.--Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide in 5N Ammonium Hydroxide Solutions Followed by Acidification in the Hydrogenations of Styrene.

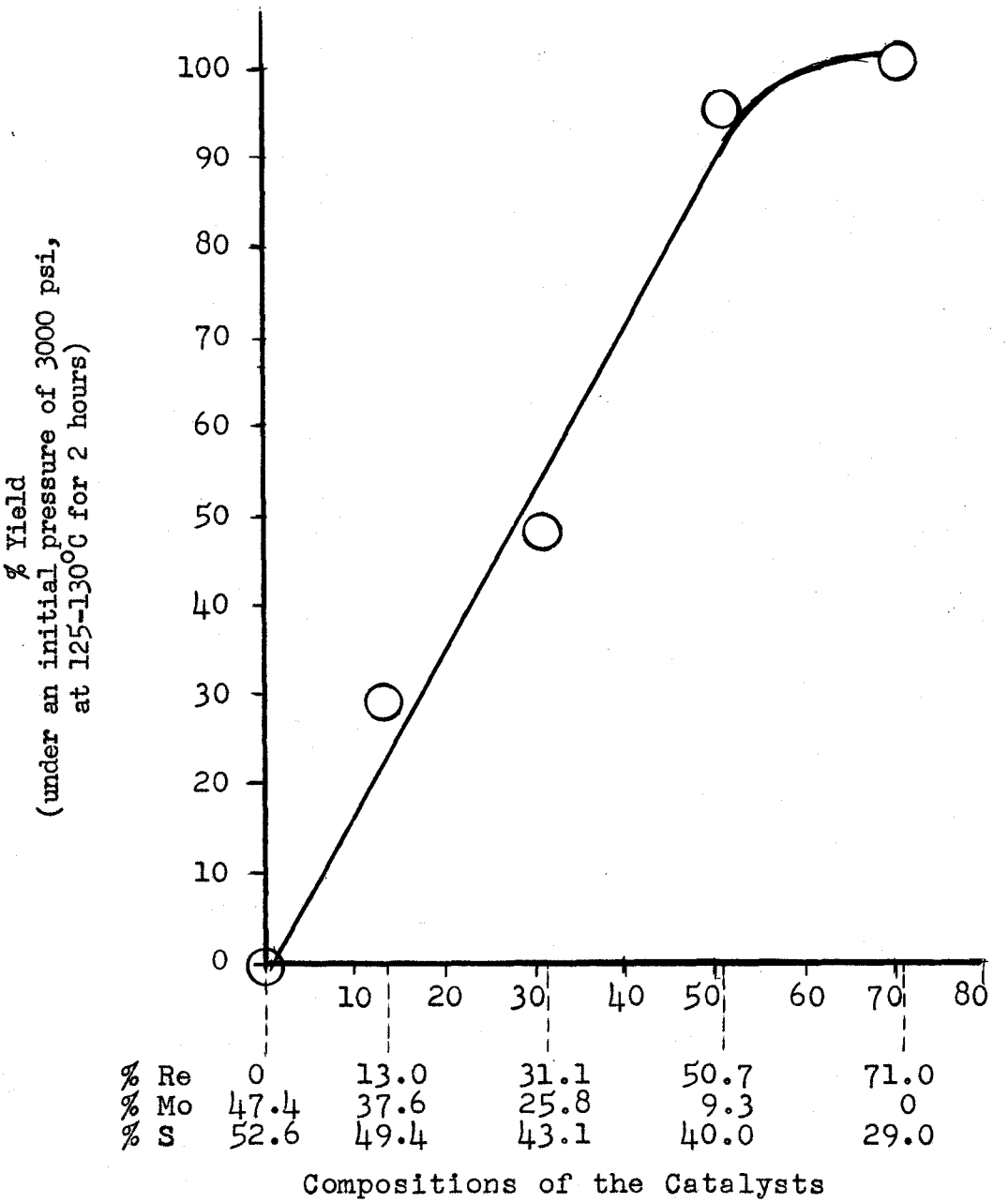


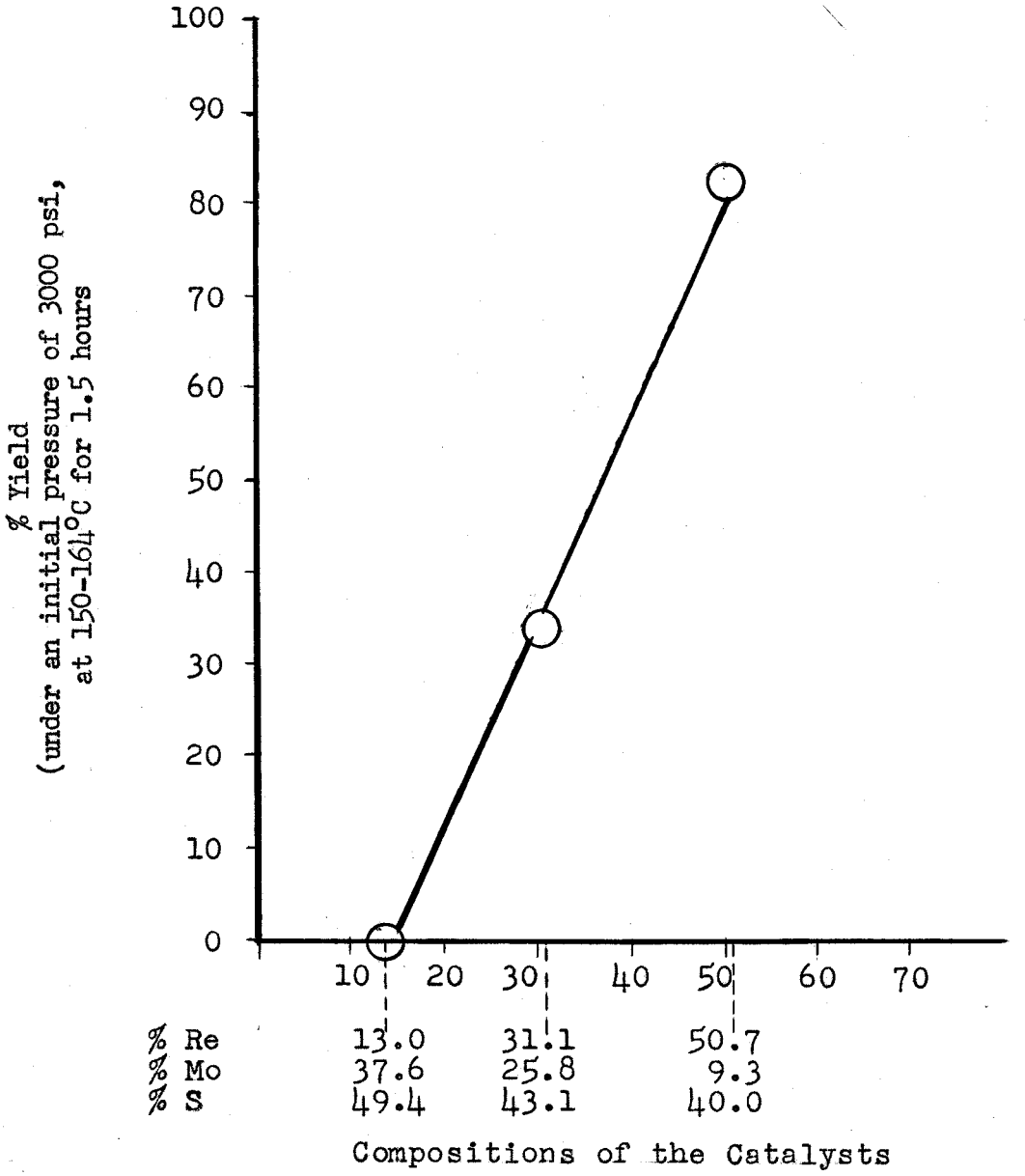
TABLE 33

Catalytic Hydrogenations of Cyclohexanone (0.2 mole) with Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts (2.5 g. per mole of Substrate) Prepared by Treating Perrhenate and and Molybdate with Hydrogen Sulfide in Ammonium Hydroxide Solutions Followed by Acidification

Catalyst Code Number	Compositions Re	Mo (%)	S	Conditions of Hydrogenation Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield	References Table No.	Batch No.
R80-M20-Ba-N2.5-4	45.3	8.8	45.9	111	3615	1.0	92	17 21	5 5
R50-M50-Ba-N2.5-4	30.8	23.3	45.9	110	3750	1.0	0	17 21	11 11
R20-M80-Ba-N2.5-4	13.0	37.8	49.2	108	3760	1.0	0	17 21	17 16
R50-M50-Ba-N2.5-4	30.8	23.3	45.9	150	3900	2.7	100	17 21	11 12
R20-M80-Ba-N2.5-4	13.0	37.8	49.2	150	4000	2.7	22	17 21	17 17
R80-M20-Ba-N5-1	50.7	9.3	40.0	150	3490	1.5	82	17 21	6 8
R50-M50-Ba-N5-1	31.1	25.8	43.1	164	4130	2.0	45 (34% for 1.5 hrs.)#	17 21	12 13
R20-M80-Ba-N5-1	13.0	37.6	49.4	152	4000	2.0	0	17 21	18 18

#The figures were deduced from the relative, experimental data by extrapolation and, therefore, are only approximate.

Fig. 13.--Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide in 5N Ammonium Hydroxide Solutions Followed by Acidification in the Hydrogenations of Cyclohexanone.



8. Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions Prepared by Treating Perrhenate and Molybdate with Thiosulfate in Dilute Sulfuric Acids.

(a) Data on the hydrogenation of nitrobenzene using this catalyst system are listed in Table 34.

From the data in Table 34, a curve with the rhenium contents of the catalysts as abscissas versus their respective catalytic activities (represented by the percentage yields of the hydrogenations) in the hydrogenations of nitrobenzene as ordinates was drawn in Fig. 14. However, the catalysts did not show any promoter action in the hydrogenations of nitrobenzene.

(b) Data on the hydrogenation of styrene using these catalyst systems are listed in Table 35.

Since the working temperature had a range of fifteen degrees, the curve drawn in Fig. 15 from the data of Table 35 was more arbitrary than others. However, the catalysts of rhenium contents of 15.4 and 22.4% seemed to possess greater catalytic activities in the hydrogenations of styrene as they did not fall as expected into the dotted line in Fig. 15. Their outstanding catalytic activities in the hydrogenations of styrene are also in comparison with those of nearly same compositions but prepared by other methods, shown in Table 39.

(c) Data on the hydrogenation of cyclohexanone using these catalyst systems appear in Table 36.

From the data in Table 36 a curve was drawn in Fig. 16. However, the catalysts did not show any promoter action in the hydrogenations of cyclohexanone.

TABLE 34

Catalytic Hydrogenations of Nitrobenzene (0.2 mole) in Ethanol (20 ml.) with Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts (2.5 g. per mole of Substrate) Prepared by Treating Perrhenate and Molybdate with Thiosulfate in Dilute Sulfuric Acids

Catalyst Code Number	Compositions Re	Mo (%)	S	Conditions of Hydrogenation Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield (Aniline)	References Table No.	Batch No.
R100-M0-T-As-4	61.8	0	38.2	73	3190	1.33	99	15 18	17 18
R80-M20-T-As-3	49.1	10.0	40.9	70	3120	1.33	92.5	17 18	8 38
R50-M50-T-As-3	35.7	23.6	40.7	72	3160	1.33	70	17 18	14 50
R20-M80-T-As-3	15.4	44.6	40.0	74	3260	1.33	57.5	17 18	21 60
R0-M100-T-As-3	0	63.2	36.8	73	2900	1.33	0	14 18	18 11

Fig. 14.--Catalytic Activities of Rhenium and Molybdenum Sulfides of Various Compositions Prepared by Treating Perrhenate and Molybdate with Thiosulfate in Dilute Sulfuric Acid Solutions in the Hydrogenations of Nitrobenzene.

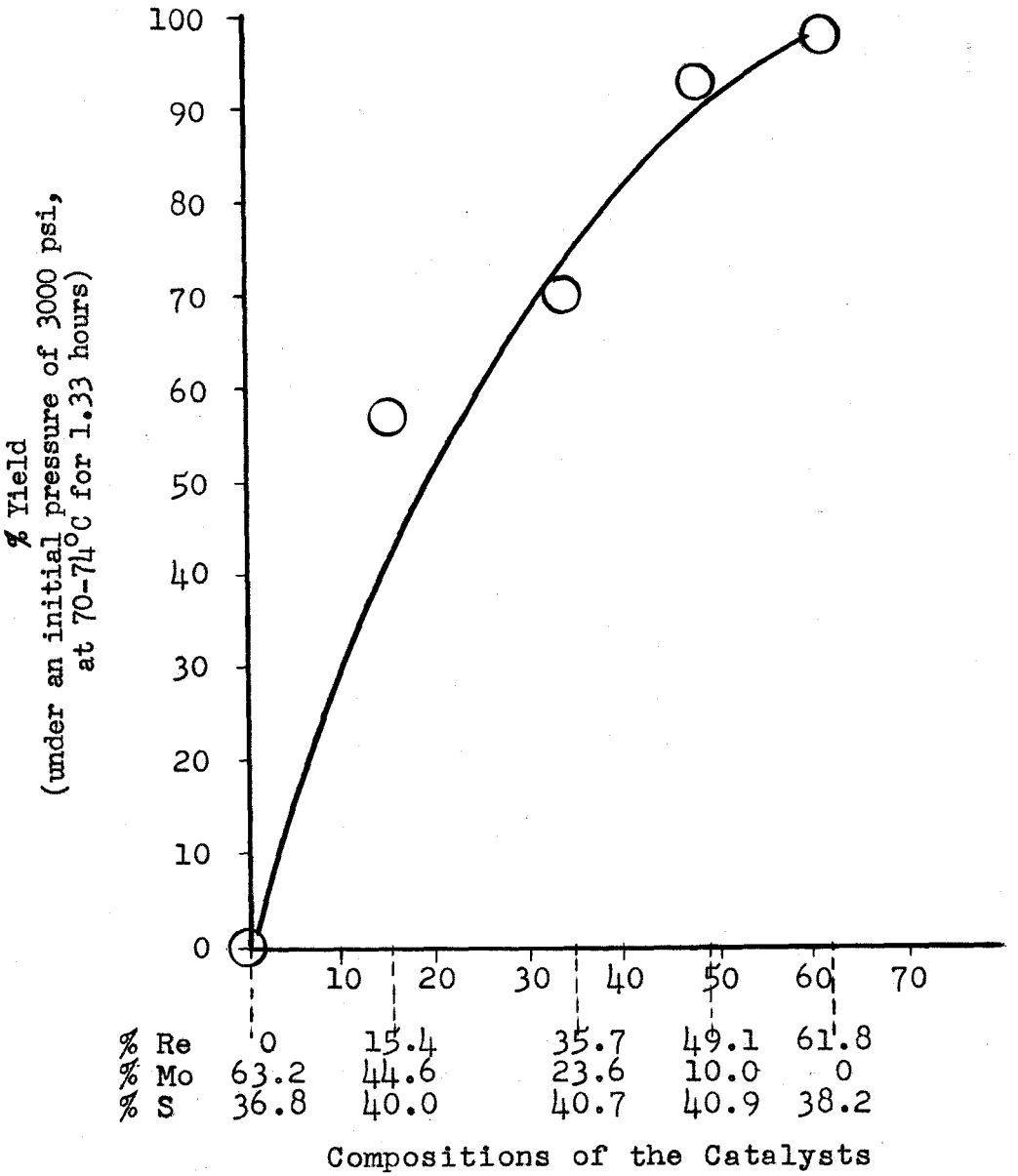


TABLE 35

Catalytic Hydrogenations of Styrene (0.2 mole) in Ethanol (20 ml.) with Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts (2.5 g. per mole of Substrate) Prepared by Treating Perrhenate and Molybdate with Thiosulfate in Dilute Sulfuric Acids

Catalyst				Conditions of Hydrogenation				References	
	Compositions			Avg.	Avg.		% Yield		
Code Number	Re	Mo (%)	S	temp. °C	pres. psi	Time hrs.	(PhC_2H_5)	Table No.	Batch No.
R80-M20-T-As-3	49.1	10.0	40.9	127	3645	1	82.5	17 20	8 15
R50-M50-T-As-3	35.7	23.6	40.7	125	3710	1	45	17 20	14 21
R20-M80-T-As-3	15.4	44.6	40.0	133	3750	1	68	17 20	21 30
R20-M80-T-As-3	15.4	44.6	40.0	140	3785	1	73.5	17 20	21 31
R20-M80-T-As-2	22.4	54.6	23.0	131	3650	1	67.5	17 20	20 29

Fig. 15.--Catalytic Activities of Rhenium and Molybdenum Sulfides of Various Compositions Prepared by Treating Perrhenate and Molybdate with Thiosulfate in Dilute Sulfuric Acid Solutions in Hydrogenations of Styrene.

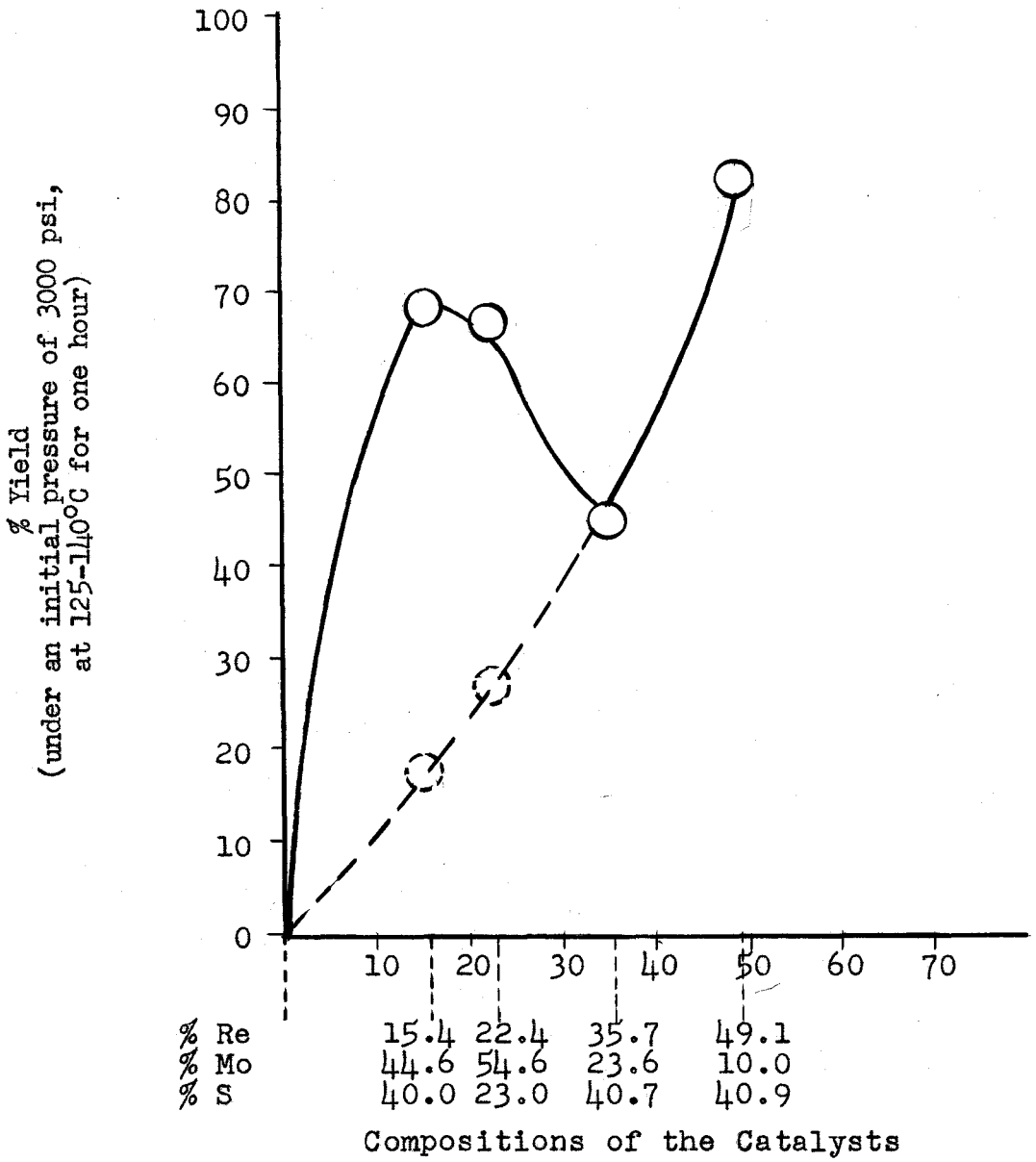
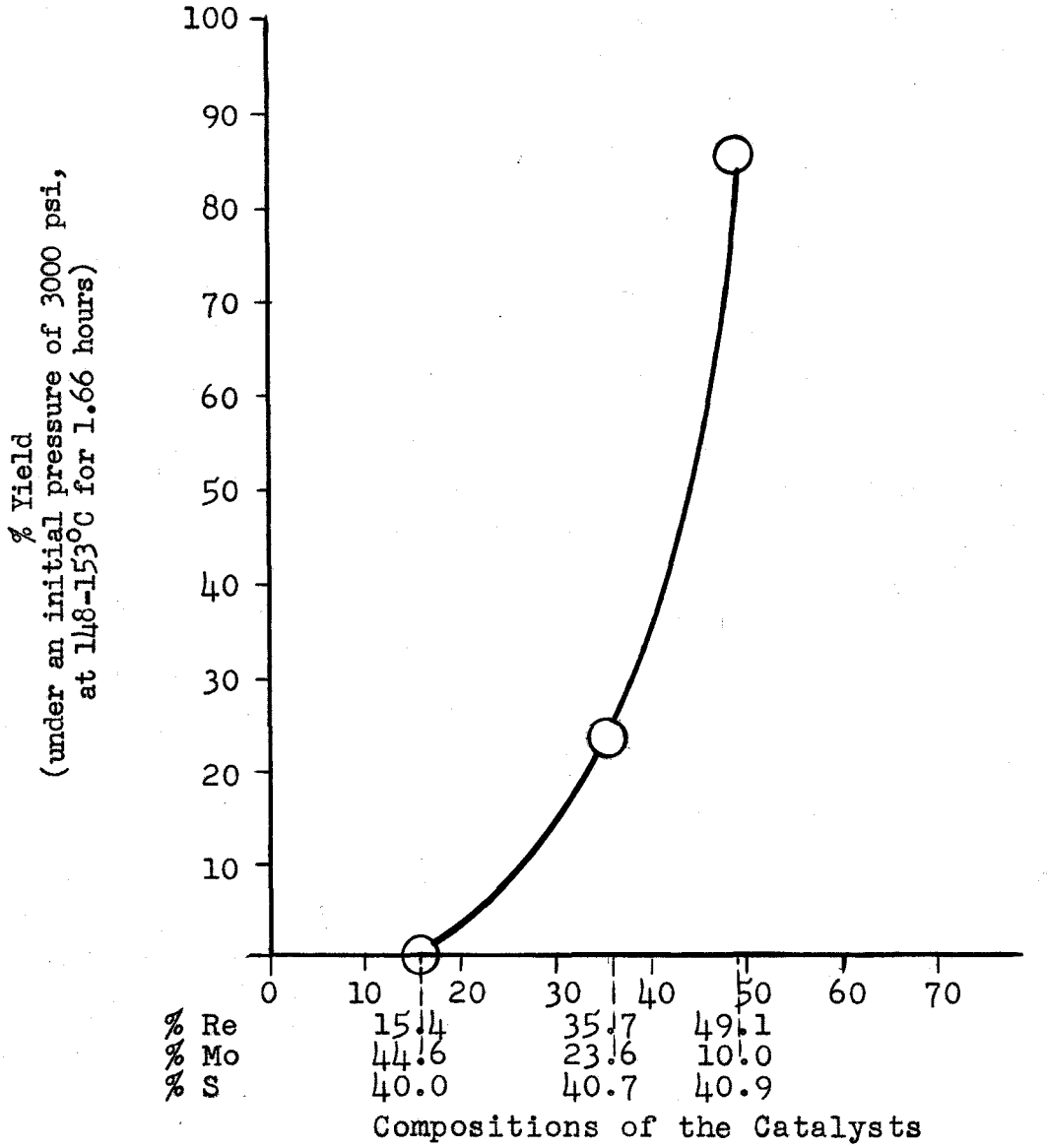


TABLE 36

Catalytic Hydrogenations of Cyclohexanone (0.2 mole) with Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts (2.5 g. per mole of Substrate) Prepared by Treating Perrhenate and Molybdate with Thiosulfate in Dilute Sulfuric Acids

Catalyst Code Number	Compositions Re	Mo (%)	S	Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield (CyOH)	References Table No.	Batch No.
R80-M20-T-As-3	49.1	10.0	40.9	148	3870	1.66	85	17 21	8 9
R50-M50-T-As-3	35.7	23.6	40.7	151	4010	1.66	23	17 21	14 14
R20-M80-T-As-3	15.4	44.6	40.0	153	4020	1.66	0	17 21	21 19

Fig. 16.--Catalytic Activities of Rhenium and Molybdenum Sulfides of Various Compositions Prepared by Treating Perrhenate and Molybdate with Thiosulfate in Dilute Sulfuric Acid Solutions in the Hydrogenations of Cyclohexanone.



9. A Comparison of Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Nearly the Same Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide but in Different Concentrations of Hydrochloric Acid Solutions in Hydrogenations of Nitrobenzene and Styrene appears in Table 37.

It seemed that the catalysts possessed greater catalytic activities when they were prepared in hydrochloric acid of higher concentrations.

10. A Comparison of Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Nearly the Same Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide but in Different Concentrations of Ammonium Hydroxide Solutions Followed by Acidification in the Hydrogenations of Nitrobenzene, Styrene, and Cyclohexanone is summarized in Table 38.

It appears that the catalysts possessed greater catalytic activities when they were prepared in ammonium hydroxide solution of lower concentrations.

11. A Comparison of Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Nearly the Same Compositions but Prepared by Different Methods in the Hydrogenations of Nitrobenzene and Styrene appears in Table 39.

From the data summarized in Table 39, general conclusions might be drawn as follows:

(a) Except for those catalysts prepared by treating perrhenate and molybdate with thiosulfate in dilute sulfuric

TABLE 37

A Comparison of Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Nearly the Same Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide but in Different Concentrations of Hydrochloric Acid Solutions in Hydrogenations of Nitrobenzene and Styrene

Catalyst					Conditions of Hydrogenation				References	
Code Number	Compositions Re	Mo (%)	S	Substrate	Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield	Table No.	Batch No.
R80-M20-Ah-N5-2	55.5	9.0	35.5	$PhNO_2$	46	2700	3.5	99	17 18	1 19
R80-M20-Ah-N2.5-4	54.5	7.5	38.0	$PhNO_2$	55	2990	5.0	61	17 18	2 22
R80-M20-Ah-N5-2	55.5	9.0	35.5	PhC_2H_3	134	3600	1	91	17 20	1 6
R80-M20-Ah-N2.5-4	54.5	7.5	38.0	PhC_2H_3	137.5	3820	1	23.5	17 20	2 9

TABLE 38

A Comparison of Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Nearly the Same Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide but in Different Concentrations of Ammonium Hydroxide Solutions Followed by Acidification in the Hydrogenations of Nitrobenzene, Styrene, and Cyclohexanone

Catalyst					Conditions of Hydrogenation					
	Compositions				Avg.	Avg.		%	References	
Code Number	Re	Mo (%)	S	Substrate	temp. °C	pres. psi	Time hrs.	Yield	Table No.	Batch No.
RO-M100-Ba-NO.25-1	0	51.1	48.9	$PhNO_2$	105	3450	3.5	23	14	12
									18	5
RO-M100-Ba-N5-1	0	47.4	52.6	"	105	3270	3.5	17	14	16
									18	10
R20-M80-Ba-N2.5-4	13.0	37.8	49.2	PhC_2H_3	124	3665	1	21.0	17	17
									20	25
R20-M80-Ba-N5-1	13.0	37.6	49.4	"	129	3800	1	14.5	17	18
									20	27
R80-M20-Ba-N2.5-4	45.3	8.8	45.9	Cy=O	115	3650	1.33	100	17	6
									21	6
R80-M20-Ba-N5-1	50.7	9.3	40.0	"	150	3490	1.5	82	17	7
									21	8
R50-M50-Ba-N2.5-4	30.8	23.3	45.9	"	150	3900	2.7	100	17	11
									21	12
R50-M50-Ba-N5-1	31.1	25.8	43.1	"	164	4130	2.0	45	17	12
									21	13
R20-M80-Ba-N2.5-4	13.0	37.8	49.2	"	150	4000	2.7	22	17	17
									21	17
R20-M80-Ba-N5-1	13.0	37.6	49.4	"	152	4000	2.0	0	17	18
									21	18

TABLE 39

A Comparison of Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Nearly the Same Compositions but Prepared by Different Methods in the Hydrogenations of Nitrobenzene and Styrene

Catalyst				Conditions of Hydrogenation						
	Compositions				Avg.	Avg.		%	References	
Code Number	Re	Mo (%)	S	Substrate	temp. °C	pres. psi	Time hrs.	Yield	Table No.	Batch No.
RO-M100-Ah-NO.25-1	0	55.4	44.6	$PhNO_2$	156	3450	11	100	14 18	9 3
RO-M100-W-NO-1	0	51.4	48.6	"	197	3820	17	100	14 18	11 4
RO-M100-T-As-3	0	63.2	36.8	"	150-175	3860	12	94.5	14 18	18 13
R80-M20-Ah-N5-2	55.5	9.0	35.5	"	46	2700	3.5	99	17 18	1 19
R80-M20-Ah-N2.5-4	54.5	7.5	38.0	"	46	3160	2.7	11	17 18	2 21
R80-M20-Ba-N2.5-4	45.3	8.8	45.9	"	45	2870	2.7	98	17 18	5 29
R80-M20-T-As-3	49.1	10.0	40.9	"	46	3140	2.7	23	17 18	8 35
R50-M50-Ah-N2.5-4	35.4	22.9	41.7	"	64	3170	4.0	31.5	17 18	10 45
R50-M50-Ba-N2.5-4	30.8	23.3	45.9	"	50	3050	2.7	84	17 18	11 47
R80-M20-Ah-N5-2	55.5	9.0	35.5	PhC_2H_3	134	3600	1	91	17 20	1 6
R80-M20-Ba-N2.5-4	45.3	8.8	45.9	"	138.5	3500	1	100	17 20	5 11

TABLE 39--Continued

Code Number	Compositions Re	Mo (%)	S	Substrate	Conditions of Hydrogenation Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield	References Table No.	Batch No.
R80-M20-Ah-N2.5-4	54.5	7.5	38.0	PhC_2H_3	122	3770	1.5	17	17 20	2 8
R80-M20-T-As-3	49.1	10.0	40.9	"	127	3645	1.0	82.5	17 20	8 15
R50-M50-Ah-N2.5-4	35.4	22.9	41.7	"	124	3760	2.2	15.5	17 20	10 18
R50-M50-Ba-N5-1	31.1	25.8	43.1	"	125	3850	2.0	48	17 20	12 20
R50-M50-T-As-3	35.7	23.6	40.7	"	125	3710	1.0	45	17 20	14 21
R20-M80-Ah-N2.5-4	19.8	33.9	46.3	"	124	3760	2.2	21.5	17 20	16 23
R20-M80-Ba-N2.5-4	13.0	37.8	49.2	"	99	3540	1	0	17 20	17 24
R20-M80-Ba-N5-1	13.0	37.6	49.4	"	129	3800	1	14.5	17 20	18 27
R20-M80-T-As-2	22.4	54.6	23.0	"	131	3650	1	67.5	17 20	20 29
R20-M80-T-As-3	15.4	44.6	40.0	"	133	3750	1	68	17 20	21 30

acids, which seemed to have special activities in the hydrogenations of styrene, in general, the catalysts prepared by treating perrhenate and molybdate with hydrogen sulfide in ammonium hydroxide solutions followed by acidification were more active for a given rhenium content than those prepared by other methods in certain ranges of catalyst composition.

(b) Methods of preparation, or rather the physical structure, seemed to be as important as the compositions of the catalysts in affecting their catalytic activities.

12. Poisoning of the Catalysts by Phosphorus.

The catalysts of code numbers R80-M20-Ah-NO.25-3 and R80-M20-Ba-NO.25-3 were contaminated with phosphorus pentoxide during the drying. Their catalytic activities seemed to be poisoned by phosphorus when they were used as catalysts in the hydrogenations of nitrobenzene. With catalysts of nearly the same compositions, hydrogenations of nitrobenzene would occur around 50°C (refer to Table 40) and would be complete in few minutes if they were carried at 90°C. However, with the catalysts contaminated with P_2O_5, no hydrogenation was found at a temperature of even up to 57-65°C for 2-3 hours, and the hydrogenations were not completed at 90°C even for more than 3 hours, as shown in Table 40.

13. Catalytic Activities of Rhenium Heptasulfide and Molybdenum Sulfide Mixed in Various Proportions in the Hydrogenations of Nitrobenzene.

Mixtures of rhenium and molybdenum sulfides prepared by treating perrhenate and molybdate with hydrogen sulfide in

TABLE 40

Poisoning of the Catalysts by Phosphorus Pentoxide in the Hydrogenations of Nitrobenzene

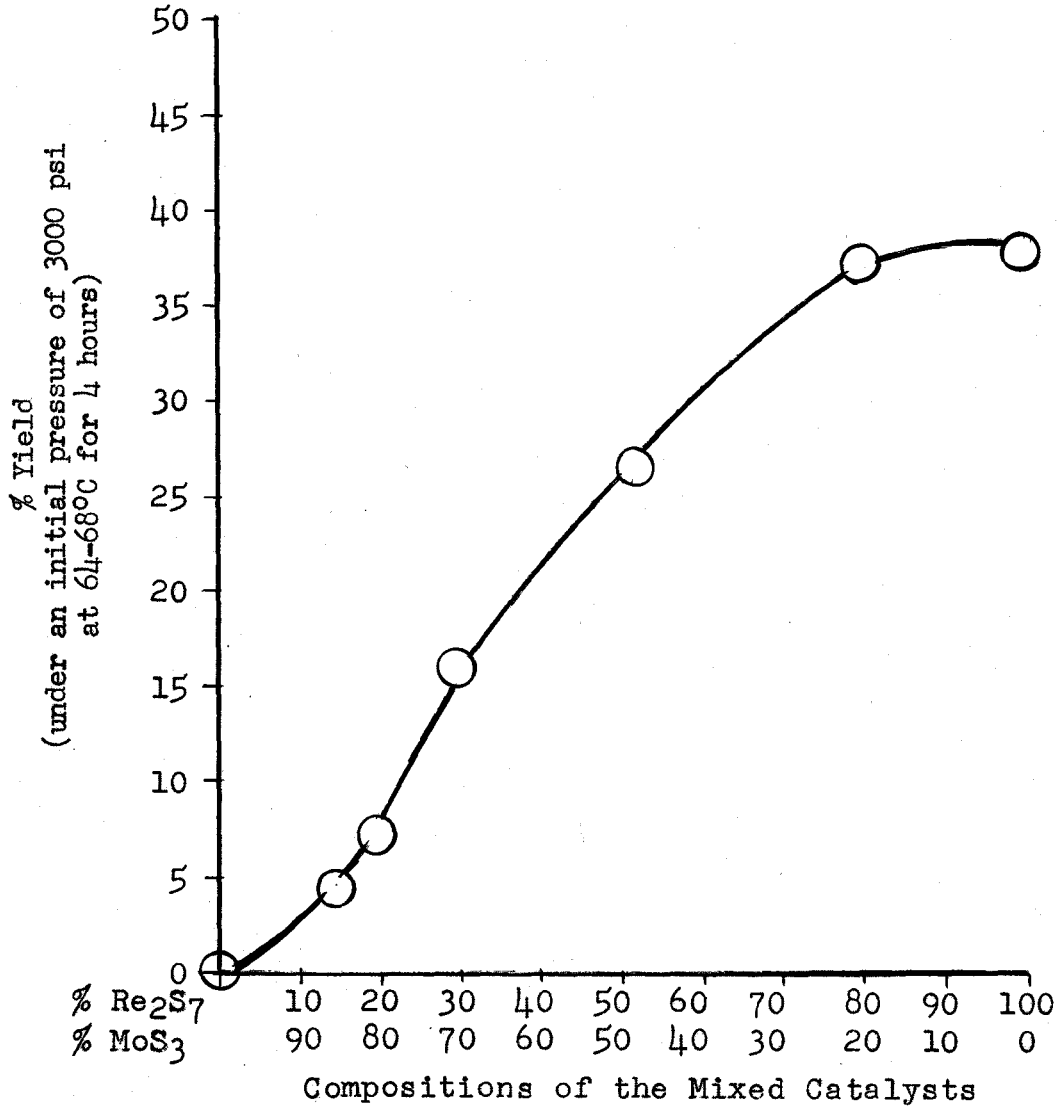
Catalyst Code Number	Compositions Re	Mo (%)	S	Conditions of Hydrogenation Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield (Aniline)	References Table No.	Batch No.
R80-M20-Ah-N2.5-4	54.5	7.5	38.0	46	3160	2.7	11	17 18	2 21
R80-M20-Ah-NO.25-3*	50.7	12.6	36.7	57	3210	2.0	0	17 18	3 25
R80-M20-Ba-N2.5-4	45.3	8.8	45.9	45	2870	2.7	98	17 18	5 29
R80-M20-Ba-NO.25-3*	50.1	10.9	39.0	65	3230	3.0	0	17 18	4 27
R80-M20-Ah-N5-2	55.5	9.0	35.5	87 (→170)	3300 (→2800)	0.05	100	17 18	1 20
R80-M20-Ah-NO.25-3*	50.7	12.6	36.7	91	3230	3.3	65.5	17 18	3 26
R80-M20-Ba-N2.5-4	45.3	8.8	45.9	60-90	3000	0.25	100	17 18	5 30
R80-M20-Ba-NO.25-3*	50.1	10.9	39.0	90	3190	3.0	76	17 18	4 28

*These catalysts were contaminated with phosphorus pentoxide.

hydrochloric acid solutions were found to have promoter actions when they were used as catalysts in the hydrogenations of nitrobenzene, styrene, and cyclohexanone. Therefore, rhenium heptasulfide of code number R100-M0-Ah-N0.25-1 (63.8% Re, 36.2% S) and molybdenum trisulfide of code number R0-M100-Ah-N2.5-4 (50.25% Mo, 49.75% S) were mixed in various proportions and used as catalysts in the hydrogenation of nitrobenzene under nearly same conditions in order to see whether they might show promoter actions.

The experimental data summarized in Table 40 were used to plot a curve in Fig. 17. However, the mixed catalysts did not show any promoter action in the hydrogenations of nitrobenzene. This result strongly suggests that the co-precipitated catalyst mixtures have peculiar structures not realized by merely mixing the two sulfides together to form a catalyst.

Fig. 17.--Catalytic Activities of Rhenium Heptasulfide (Code Number R100-MO-Ah-NO.25-1) and Molybdenum Trisulfide (Code Number RO-M100-Ah-N2.5-4) Mixed in Various Proportions.



V. SUMMARY AND CONCLUSIONS

1. Catalytic activities of mixtures of rhenium and molybdenum sulfides of various compositions prepared by three different methods were investigated in the hydrogenations of nitrobenzene, styrene, and cyclohexanone.

2. Mixtures of the sulfides prepared by saturating perrhenate and molybdate with hydrogen sulfide in hydrochloric acid solutions were found to have promoter actions in the hydrogenations of all the three substrates. Their catalytic activities seemed to be greater if they were prepared in hydrochloric acid solutions of higher concentration.

3. Those sulfide mixtures prepared by treating perrhenate and molybdate with thiosulfate in dilute sulfuric acid solutions were found to have promoter action only in the hydrogenations of styrene, but not of the others.

4. Those sulfide mixtures prepared by saturating perrhenate and molybdate with hydrogen sulfide in ammonium hydroxide solutions followed by acidification were not found to have any promoter action in the hydrogenations of any of the three substrates. Their catalytic activities seemed to be greater if they were prepared in ammonium hydroxide solutions of lower concentrations. For comparable rhenium content they were found, in general, to have greater catalytic activities than those prepared by the other methods in certain ranges of catalyst composition.

5. Pure rhenium heptasulfide and pure molybdenum trisulfide were also prepared by saturating their corresponding salts with hydrogen sulfide in hydrochloric acid solutions. The catalytic activities of the pure sulfides mixed in various proportions were also investigated in the hydrogenation of nitrobenzene. However, they were not found to have any promoter action, i.e., the activities of the mixtures could be predicted by simple dilution laws.

6. Mixtures of rhenium and molybdenum sulfides were found to be poisoned by phosphorus pentoxide in the hydrogenations of nitrobenzene.

7. In the precipitation of pure rhenium heptasulfide or molybdenum sulfide by saturating the respective salt with hydrogen sulfide, rhenium heptasulfide was found to precipitate more completely in hydrochloric acid solution of higher concentrations and slower and less completely in ammonium hydroxide solutions unless followed by acidification. Molybdenum sulfide was found to precipitate more incompletely in hydrochloric acid solution of higher concentrations and entirely not in ammonium hydroxide solutions unless followed by acidification.

8. Of the three methods for the preparations of mixtures of rhenium and molybdenum sulfides, the one by saturating perrhenate and molybdate with hydrogen sulfide in fairly concentrated ammonium hydroxide solutions followed by acidification was found to give the most satisfactory yields.

9. In the extraction of mixtures of the sulfides by

toluene, free sulfur and finally molybdenum sulfide and even rhenium heptasulfide could be extracted by prolonged treatment.

10. Mixtures of the sulfides were found to be brought into solution more conveniently with 30% hydrogen peroxide in alkaline solutions than with sodium peroxide fusion, with bromine and nitric acid, or with mixtures of nitric and sulfuric acids.

11. Molybdenum in pure molybdenum sulfide was found to be determined satisfactorily by either the permanganate titration or the α-benzoinoxime precipitation method. Molybdenum in the presence of rhenium could be determined by either the α-benzoinoxime precipitation or the lead molybdate precipitation method.

12. The determination of rhenium in either pure rhenium sulfide or mixtures of molybdenum and rhenium sulfides was found to be more satisfactorily accomplished by precipitation with tetraphenylarsonium chloride in 6M ammonium hydroxide solution than in 5% hydrochloric acid or in 0.6M tartaric acid solution.

13. The physical structure of the catalysts was found to be as important as their compositions in determining their catalytic activities in hydrogenations.

14. It might be beneficial to the hydrogenation industries to search out the effective compositions of mixtures of rhenium and molybdenum sulfides which would be expected to have maximum catalytic activities in hydrogenations.

TABLE 35

Catalytic Hydrogenations of Styrene (0.2 mole) in Ethanol (20 ml.) with Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts (2.5 g. per mole of Substrate) Prepared by Treating Perrhenate and Molybdate with Thiosulfate in Dilute Sulfuric Acids

Catalyst				Conditions of Hydrogenation					
	Compositions			Avg.	Avg.		% Yield	References	
Code Number	Re	Mo (%)	S	temp. °C	pres. psi	Time hrs.	(PhC_2H_5)	Table No.	Batch No.
R80-M20-T-As-3	49.1	10.0	40.9	127	3645	1	82.5	17 20	8 15
R50-M50-T-As-3	35.7	23.6	40.7	125	3710	1	45	17 20	14 21
R20-M80-T-As-3	15.4	44.6	40.0	133	3750	1	68	17 20	21 30
R20-M80-T-As-3	15.4	44.6	40.0	140	3785	1	73.5	17 20	21 31
R20-M80-T-As-2	22.4	54.6	23.0	131	3650	1	67.5	17 20	20 29

Fig. 15.--Catalytic Activities of Rhenium and Molybdenum Sulfides of Various Compositions Prepared by Treating Perrhenate and Molybdate with Thiosulfate in Dilute Sulfuric Acid Solutions in Hydrogenations of Styrene.

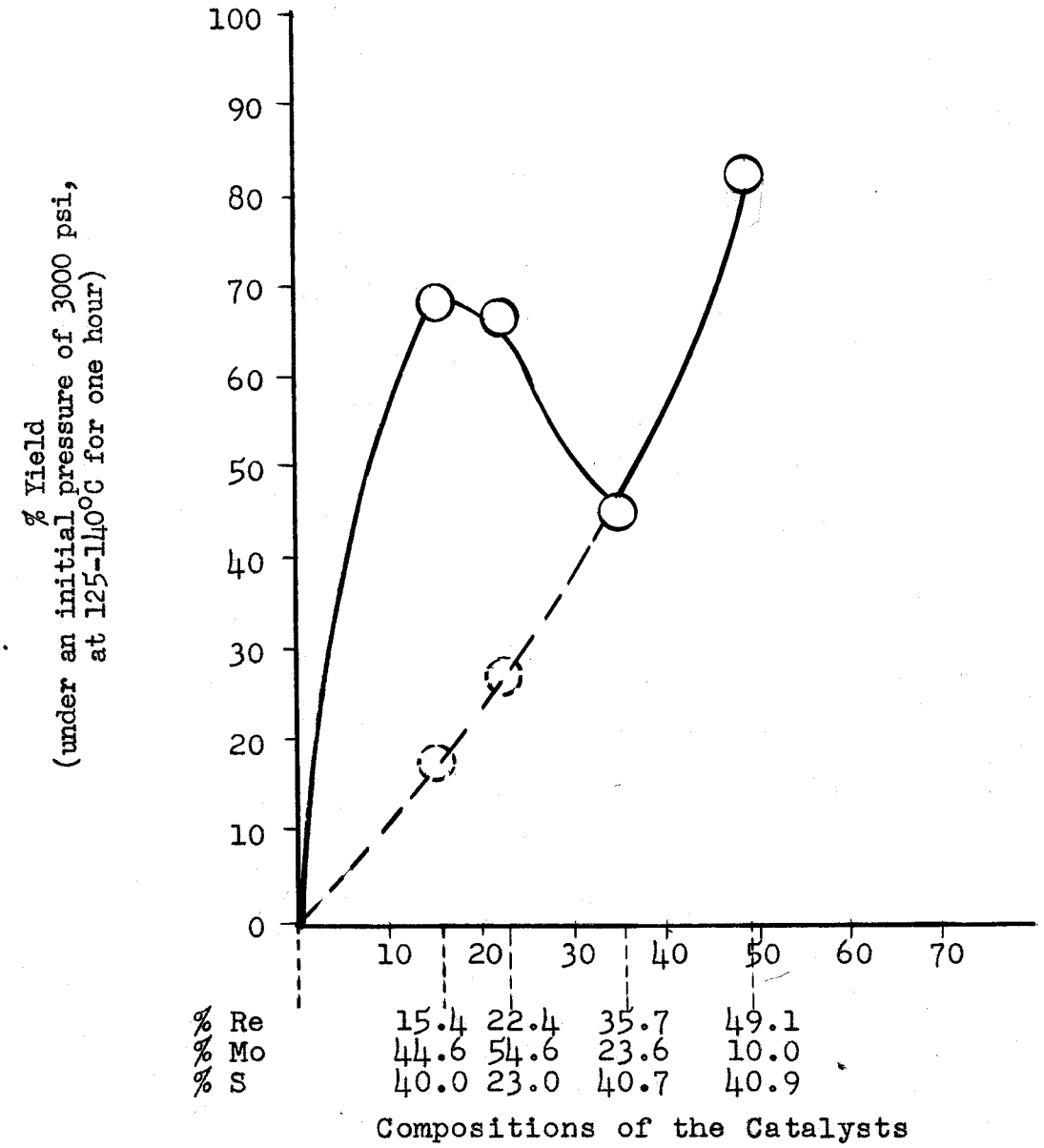
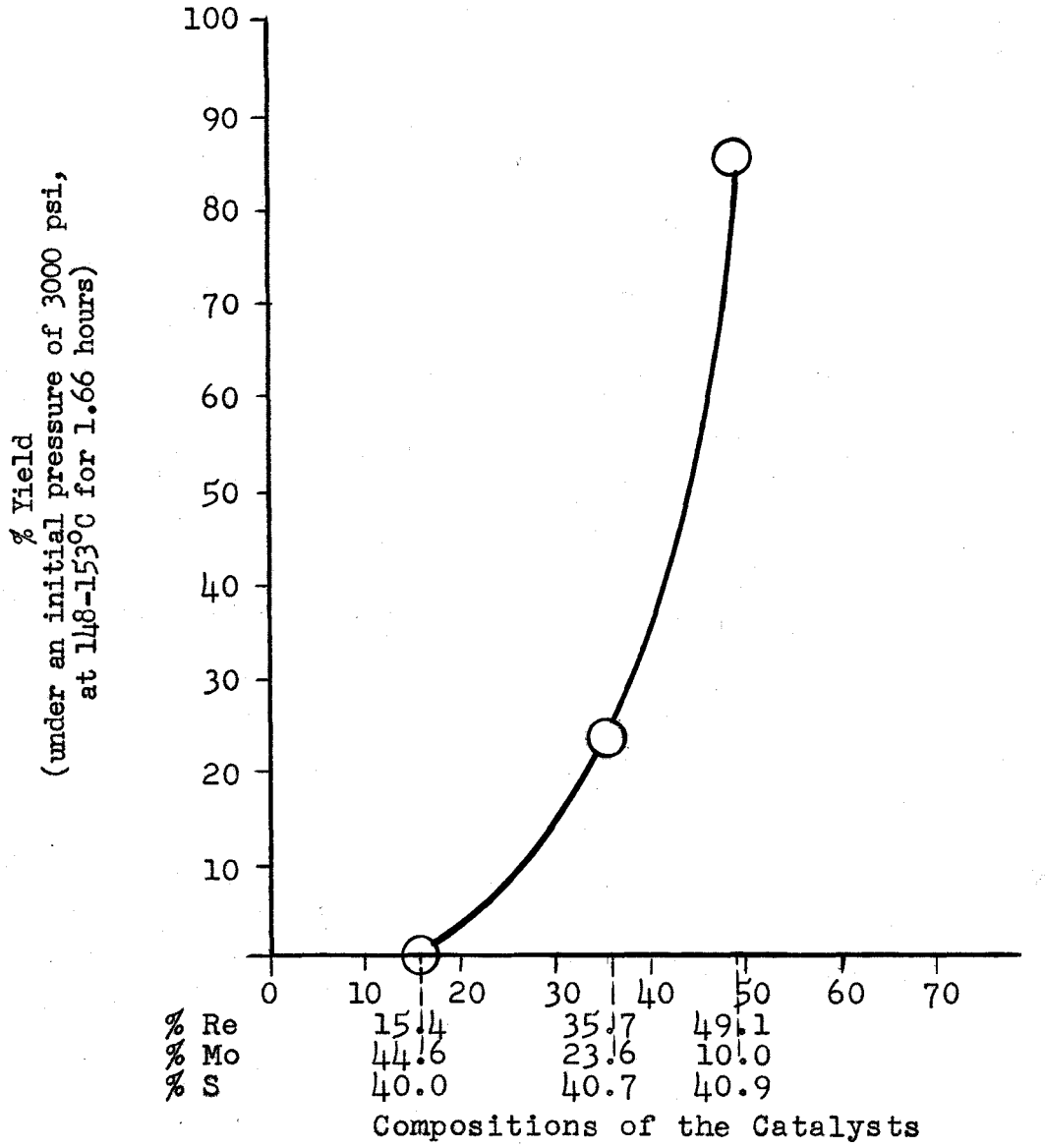


TABLE 36

Catalytic Hydrogenations of Cyclohexanone (0.2 mole) with Mixtures of Rhenium and Molybdenum Sulfides of Various Compositions as Catalysts (2.5 g. per mole of Substrate) Prepared by Treating Perrhenate and Molybdate with Thiosulfate in Dilute Sulfuric Acids

Catalyst Code Number	Compositions Re	Mo (%)	S	Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield (CyOH)	References Table No.	Batch No.
R80-M20-T-As-3	49.1	10.0	40.9	148	3870	1.66	85	17 21	8 9
R50-M50-T-As-3	35.7	23.6	40.7	151	4010	1.66	23	17 21	14 14
R20-M80-T-As-3	15.4	44.6	40.0	153	4020	1.66	0	17 21	21 19

Fig. 16.--Catalytic Activities of Rhenium and Molybdenum Sulfides of Various Compositions Prepared by Treating Perrhenate and Molybdate with Thiosulfate in Dilute Sulfuric Acid Solutions in the Hydrogenations of Cyclohexanone.



9. A Comparison of Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Nearly the Same Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide but in Different Concentrations of Hydrochloric Acid Solutions in Hydrogenations of Nitrobenzene and Styrene appears in Table 37.

It seemed that the catalysts possessed greater catalytic activities when they were prepared in hydrochloric acid of higher concentrations.

10. A Comparison of Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Nearly the Same Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide but in Different Concentrations of Ammonium Hydroxide Solutions Followed by Acidification in the Hydrogenations of Nitrobenzene, Styrene, and Cyclohexanone is summarized in Table 38.

It appears that the catalysts possessed greater catalytic activities when they were prepared in ammonium hydroxide solution of lower concentrations.

11. A Comparison of Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Nearly the Same Compositions but Prepared by Different Methods in the Hydrogenations of Nitrobenzene and Styrene appears in Table 39.

From the data summarized in Table 39, general conclusions might be drawn as follows:

(a) Except for those catalysts prepared by treating perrhenate and molybdate with thiosulfate in dilute sulfuric

TABLE 37

A Comparison of Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Nearly the Same Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide but in Different Concentrations of Hydrochloric Acid Solutions in Hydrogenations of Nitrobenzene and Styrene

Catalyst					Conditions of Hydrogenation				References	
Code Number	Compositions Re	Mo (%)	S	Substrate	Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield	Table No.	Batch No.
R80-M20-Ah-N5-2	55.5	9.0	35.5	$PhNO_2$	46	2700	3.5	99	17 18	1 19
R80-M20-Ah-N2.5-4	54.5	7.5	38.0	$PhNO_2$	55	2990	5.0	61	17 18	2 22
R80-M20-Ah-N5-2	55.5	9.0	35.5	PhC_2H_3	134	3600	1	91	17 20	1 6
R80-M20-Ah-N2.5-4	54.5	7.5	38.0	PhC_2H_3	137.5	3820	1	23.5	17 20	2 9

TABLE 38

A Comparison of Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Nearly the Same Compositions Prepared by Treating Perrhenate and Molybdate with Hydrogen Sulfide but in Different Concentrations of Ammonium Hydroxide Solutions Followed by Acidification in the Hydrogenations of Nitrobenzene, Styrene, and Cyclohexanone

Catalyst				Conditions of Hydrogenation						
	Compositions				Avg.	Avg.		%	References	
Code Number	Re	Mo (%)	S	Substrate	temp. °C	pres. psi	Time hrs.	Yield	Table No.	Batch No.
R0-M100-Ba-N0.25-1	0	51.1	48.9	$PhNO_2$	105	3450	3.5	23	14	12
									18	5
R0-M100-Ba-N5-1	0	47.4	52.6	"	105	3270	3.5	17	14	16
									18	10
R20-M80-Ba-N2.5-4	13.0	37.8	49.2	PhC_2H_3	124	3665	1	21.0	17	17
									20	25
R20-M80-Ba-N5-1	13.0	37.6	49.4	"	129	3800	1	14.5	17	18
									20	27
R80-M20-Ba-N2.5-4	45.3	8.8	45.9	Cy=O	115	3650	1.33	100	17	6
									21	6
R80-M20-Ba-N5-1	50.7	9.3	40.0	"	150	3490	1.5	82	17	7
									21	8
R50-M50-Ba-N2.5-4	30.8	23.3	45.9	"	150	3900	2.7	100	17	11
									21	12
R50-M50-Ba-N5-1	31.1	25.8	43.1	"	164	4130	2.0	45	17	12
									21	13
R20-M80-Ba-N2.5-4	13.0	37.8	49.2	"	150	4000	2.7	22	17	17
									21	17
R20-M80-Ba-N5-1	13.0	37.6	49.4	"	152	4000	2.0	0	17	18
									21	18

TABLE 39

A Comparison of Catalytic Activities of Mixtures of Rhenium and Molybdenum Sulfides of Nearly the Same Compositions but Prepared by Different Methods in the Hydrogenations of Nitrobenzene and Styrene

Catalyst				Conditions of Hydrogenation						
	Compositions				Avg.	Avg.		%	References	
Code Number	Re	Mo (%)	S	Substrate	temp. °C	pres. psi	Time hrs.	Yield	Table No.	Batch No.
RO-M100-Ah-NO.25-1	0	55.4	44.6	$PhNO_2$	156	3450	11	100	14 18	9 3
RO-M100-W-NO-1	0	51.4	48.6	"	197	3820	17	100	14 18	11 4
RO-M100-T-As-3	0	63.2	36.8	"	150-175	3860	12	94.5	14 18	18 13
R80-M20-Ah-N5-2	55.5	9.0	35.5	"	46	2700	3.5	99	17 18	1 19
R80-M20-Ah-N2.5-4	54.5	7.5	38.0	"	46	3160	2.7	11	17 18	2 21
R80-M20-Ba-N2.5-4	45.3	8.8	45.9	"	45	2870	2.7	98	17 18	5 29
R80-M20-T-As-3	49.1	10.0	40.9	"	46	3140	2.7	23	17 18	8 35
R50-M50-Ah-N2.5-4	35.4	22.9	41.7	"	64	3170	4.0	31.5	17 18	10 45
R50-M50-Ba-N2.5-4	30.8	23.3	45.9	"	50	3050	2.7	84	17 18	11 47
R80-M20-Ah-N5-2	55.5	9.0	35.5	PhC_2H_3	134	3600	1	91	17 20	1 6
R80-M20-Ba-N2.5-4	45.3	8.8	45.9	"	138.5	3500	1	100	17 20	5 11

TABLE 39--Continued

Code Number	Compositions Re	Mo (%)	S	Substrate	Conditions of Hydrogenation Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield	References Table No.	Batch No.
R80-M20-Ah-N2.5-4	54.5	7.5	38.0	PhC_2H_3	122	3770	1.5	17	17 20	2 8
R80-M20-T-As-3	49.1	10.0	40.9	"	127	3645	1.0	82.5	17 20	8 15
R50-M50-Ah-N2.5-4	35.4	22.9	41.7	"	124	3760	2.2	15.5	17 20	10 18
R50-M50-Ba-N5-1	31.1	25.8	43.1	"	125	3850	2.0	48	17 20	12 20
R50-M50-T-As-3	35.7	23.6	40.7	"	125	3710	1.0	45	17 20	14 21
R20-M80-Ah-N2.5-4	19.8	33.9	46.3	"	124	3760	2.2	21.5	17 20	16 23
R20-M80-Ba-N2.5-4	13.0	37.8	49.2	"	99	3540	1	0	17 20	17 24
R20-M80-Ba-N5-1	13.0	37.6	49.4	"	129	3800	1	14.5	17 20	18 27
R20-M80-T-As-2	22.4	54.6	23.0	"	131	3650	1	67.5	17 20	20 29
R20-M80-T-As-3	15.4	44.6	40.0	"	133	3750	1	68	17 20	21 30

acids, which seemed to have special activities in the hydrogenations of styrene, in general, the catalysts prepared by treating perrhenate and molybdate with hydrogen sulfide in ammonium hydroxide solutions followed by acidification were more active for a given rhenium content than those prepared by other methods in certain ranges of catalyst composition.

(b) Methods of preparation, or rather the physical structure, seemed to be as important as the compositions of the catalysts in affecting their catalytic activities.

12. Poisoning of the Catalysts by Phosphorus.

The catalysts of code numbers R80-M20-Ah-NO.25-3 and R80-M20-Ba-NO.25-3 were contaminated with phosphorus pentoxide during the drying. Their catalytic activities seemed to be poisoned by phosphorus when they were used as catalysts in the hydrogenations of nitrobenzene. With catalysts of nearly the same compositions, hydrogenations of nitrobenzene would occur around 50°C (refer to Table 40) and would be complete in few minutes if they were carried at 90°C. However, with the catalysts contaminated with P_2O_5, no hydrogenation was found at a temperature of even up to 57-65°C for 2-3 hours, and the hydrogenations were not completed at 90°C even for more than 3 hours, as shown in Table 40.

13. Catalytic Activities of Rhenium Heptasulfide and Molybdenum Sulfide Mixed in Various Proportions in the Hydrogenations of Nitrobenzene.

Mixtures of rhenium and molybdenum sulfides prepared by treating perrhenate and molybdate with hydrogen sulfide in

TABLE 40

Poisoning of the Catalysts by Phosphorus Pentoxide in the Hydrogenations of Nitrobenzene

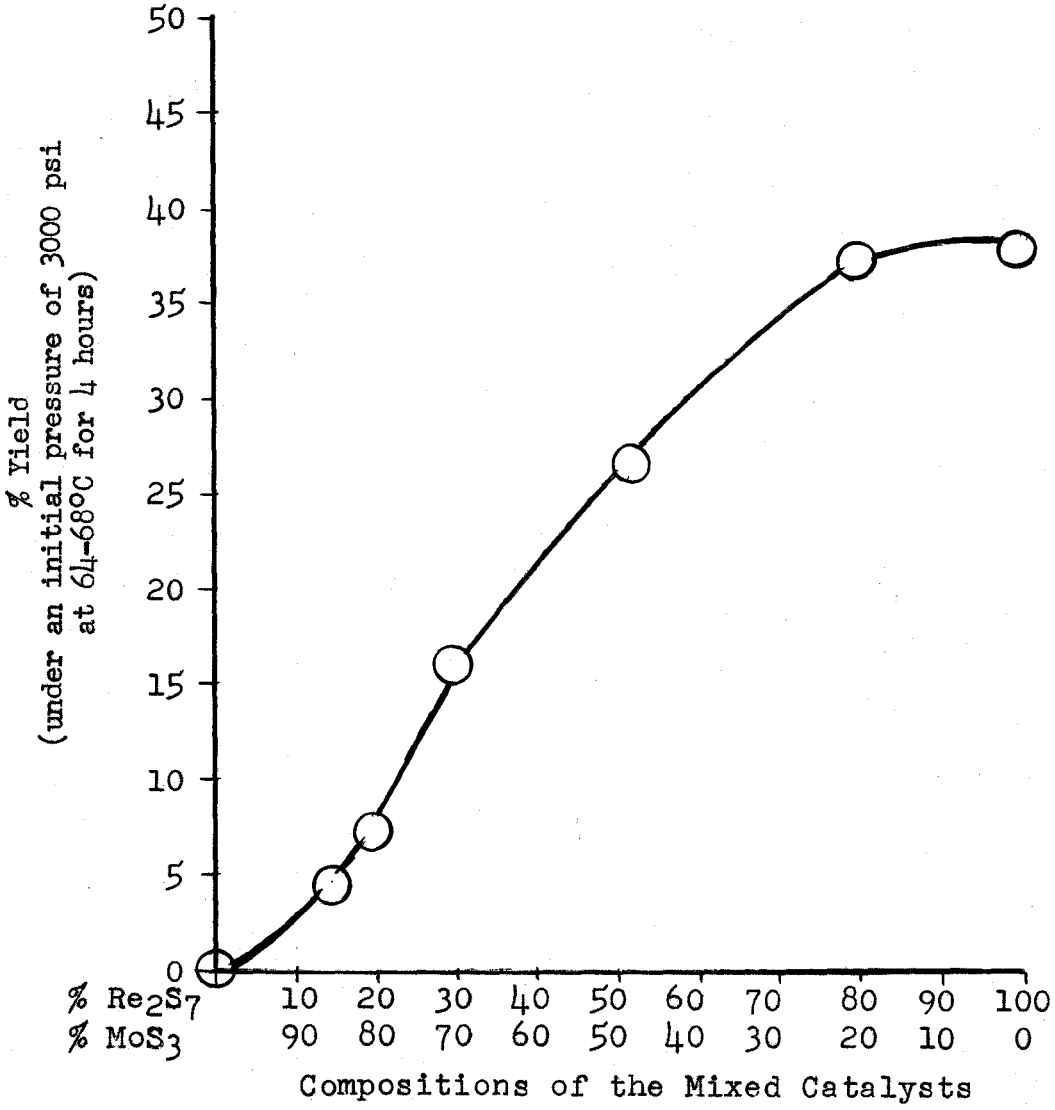
Catalyst Code Number	Compositions Re	Mo (%)	S	Conditions of Hydrogenation Avg. temp. °C	Avg. pres. psi	Time hrs.	% Yield (Aniline)	References Table No.	Batch No.
R80-M20-Ah-N2.5-4	54.5	7.5	38.0	46	3160	2.7	11	17 18	2 21
R80-M20-Ah-NO.25-3*	50.7	12.6	36.7	57	3210	2.0	0	17 18	3 25
R80-M20-Ba-N2.5-4	45.3	8.8	45.9	45	2870	2.7	98	17 18	5 29
R80-M20-Ba-NO.25-3*	50.1	10.9	39.0	65	3230	3.0	0	17 18	4 27
R80-M20-Ah-N5-2	55.5	9.0	35.5	87 (→170)	3300 (→2800)	0.05	100	17 18	1 20
R80-M20-Ah-NO.25-3*	50.7	12.6	36.7	91	3230	3.3	65.5	17 18	3 26
R80-M20-Ba-N2.5-4	45.3	8.8	45.9	60-90	3000	0.25	100	17 18	5 30
R80-M20-Ba-NO.25-3*	50.1	10.9	39.0	90	3190	3.0	76	17 18	4 28

*These catalysts were contaminated with phosphorus pentoxide.

hydrochloric acid solutions were found to have promoter actions when they were used as catalysts in the hydrogenations of nitrobenzene, styrene, and cyclohexanone. Therefore, rhenium heptasulfide of code number R100-M0-Ah-N0.25-1 (63.8% Re, 36.2% S) and molybdenum trisulfide of code number R0-M100-Ah-N2.5-4 (50.25% Mo, 49.75% S) were mixed in various proportions and used as catalysts in the hydrogenation of nitrobenzene under nearly same conditions in order to see whether they might show promoter actions.

The experimental data summarized in Table 40 were used to plot a curve in Fig. 17. However, the mixed catalysts did not show any promoter action in the hydrogenations of nitrobenzene. This result strongly suggests that the co-precipitated catalyst mixtures have peculiar structures not realized by merely mixing the two sulfides together to form a catalyst.

Fig. 17.--Catalytic Activities of Rhenium Heptasulfide (Code Number R100-MO-Ah-NO.25-1) and Molybdenum Trisulfide (Code Number RO-M100-Ah-N2.5-4) Mixed in Various Proportions.



V. SUMMARY AND CONCLUSIONS

1. Catalytic activities of mixtures of rhenium and molybdenum sulfides of various compositions prepared by three different methods were investigated in the hydrogenations of nitrobenzene, styrene, and cyclohexanone.

2. Mixtures of the sulfides prepared by saturating perrhenate and molybdate with hydrogen sulfide in hydrochloric acid solutions were found to have promoter actions in the hydrogenations of all the three substrates. Their catalytic activities seemed to be greater if they were prepared in hydrochloric acid solutions of higher concentration.

3. Those sulfide mixtures prepared by treating perrhenate and molybdate with thiosulfate in dilute sulfuric acid solutions were found to have promoter action only in the hydrogenations of styrene, but not of the others.

4. Those sulfide mixtures prepared by saturating perrhenate and molybdate with hydrogen sulfide in ammonium hydroxide solutions followed by acidification were not found to have any promoter action in the hydrogenations of any of the three substrates. Their catalytic activities seemed to be greater if they were prepared in ammonium hydroxide solutions of lower concentrations. For comparable rhenium content they were found, in general, to have greater catalytic activities than those prepared by the other methods in certain ranges of catalyst composition.

5. Pure rhenium heptasulfide and pure molybdenum trisulfide were also prepared by saturating their corresponding salts with hydrogen sulfide in hydrochloric acid solutions. The catalytic activities of the pure sulfides mixed in various proportions were also investigated in the hydrogenation of nitrobenzene. However, they were not found to have any promoter action, i.e., the activities of the mixtures could be predicted by simple dilution laws.

6. Mixtures of rhenium and molybdenum sulfides were found to be poisoned by phosphorus pentoxide in the hydrogenations of nitrobenzene.

7. In the precipitation of pure rhenium heptasulfide or molybdenum sulfide by saturating the respective salt with hydrogen sulfide, rhenium heptasulfide was found to precipitate more completely in hydrochloric acid solution of higher concentrations and slower and less completely in ammonium hydroxide solutions unless followed by acidification. Molybdenum sulfide was found to precipitate more incompletely in hydrochloric acid solution of higher concentrations and entirely not in ammonium hydroxide solutions unless followed by acidification.

8. Of the three methods for the preparations of mixtures of rhenium and molybdenum sulfides, the one by saturating perrhenate and molybdate with hydrogen sulfide in fairly concentrated ammonium hydroxide solutions followed by acidification was found to give the most satisfactory yields.

9. In the extraction of mixtures of the sulfides by

toluene, free sulfur and finally molybdenum sulfide and even rhenium heptasulfide could be extracted by prolonged treatment.

10. Mixtures of the sulfides were found to be brought into solution more conveniently with 30% hydrogen peroxide in alkaline solutions than with sodium peroxide fusion, with bromine and nitric acid, or with mixtures of nitric and sulfuric acids.

11. Molybdenum in pure molybdenum sulfide was found to be determined satisfactorily by either the permanganate titration or the α-benzoinoxime precipitation method. Molybdenum in the presence of rhenium could be determined by either the α-benzoinoxime precipitation or the lead molybdate precipitation method.

12. The determination of rhenium in either pure rhenium sulfide or mixtures of molybdenum and rhenium sulfides was found to be more satisfactorily accomplished by precipitation with tetraphenylarsonium chloride in 6M ammonium hydroxide solution than in 5% hydrochloric acid or in 0.6M tartaric acid solution.

13. The physical structure of the catalysts was found to be as important as their compositions in determining their catalytic activities in hydrogenations.

14. It might be beneficial to the hydrogenation industries to search out the effective compositions of mixtures of rhenium and molybdenum sulfides which would be expected to have maximum catalytic activities in hydrogenations.

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A CORRELATION OF THE CATALYTIC ACTIVITY OF VARIOUS MIXTURES OF RHENIUM AND MOLYBDENUM SULFIDES IN LIQUID-PHASE HYDROGENATION OF CERTAIN REDUCIBLE ORGANIC GROUPS

An Abstract

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Master of Science

by

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ABSTRACT

The promoter action of mixtures of catalysts has been reported in literature to be valuable in industries. Whether mixtures of rhenium and molybdenum sulfides would have promoter actions in the hydrogenations of certain reducible organic groups was the main object of this research.

Mixtures of rhenium and molybdenum sulfides of various compositions were prepared by three different methods, i.e., (a) by saturating perrhenate and molybdate with hydrogen sulfide in hydrochloric acid solutions, (b) in ammonium hydroxide solutions followed by acidification, and (c) by treating perrhenate and molybdate with thiosulfate in dilute sulfuric acids followed by extraction with toluene to remove excess sulfur. Those prepared in ammonium hydroxide solutions (greater than 2.5N) followed by acidification were found to have satisfactory yields.

After drying to the constant weight over phosphorus pentoxide under a vacuum of 50-100 microns at about 150°C, the mixtures were brought into solution with 30% hydrogen peroxide in alkaline solutions. The rhenium contents were determined by precipitation with tetraphenylarsonium chloride in 6M ammonium hydroxide solutions. The molybdenum contents were determined by the α-benzoinoxime precipitation method, or alternatively, the permanganate titration method if the solutions contained only molybdenum compounds. The sulfur contents

were determined by the barium sulfate method. The compositions of all the mixtures of rhenium and molybdenum sulfides except those having received prolonged extraction with toluene were found to be not far from, though not coincident with, their respective calculated values.

The catalytic activities of mixtures of the sulfides of various compositions prepared by the three different methods were investigated in the hydrogenations of nitrobenzene (nitro group), styrene (carbon to carbon double bond conjugated with a benzene ring), and cyclohexanone (carbon to oxygen double bond). Those prepared by the second method were not found to have any promoter action in the hydrogenation of any of the three substrates. Those prepared by the third method were found to have promoter action only in the hydrogenation of styrene but not of the others. Those prepared by the first method were found to have promoter actions in the hydrogenations of all the three substrates.

The catalytic activities of pure rhenium heptasulfide and pure molybdenum trisulfide (both prepared by the first (a) method) mixed in various proportions were also investigated in the hydrogenations of nitrobenzene. However, they did not show any promoter action. Furthermore, mixtures of the sulfides of nearly same compositions but prepared by different methods and even by the same methods but in solutions of different pH were found to possess markably different catalytic activities in hydrogenations.

From these facts a conclusion might be drawn that the

physical structure of the catalysts as well as their compositions plays an important role in their catalytic activities in hydrogenations. It would be beneficial to the hydrogenation industries to search out the effective compositions of mixtures of rhenium and molybdenum sulfides prepared by the first method which would have maximum catalytic activities in hydrogenation reactions.