satisfactory method. The problem of obtaining exact concentrations of carbon dioxide and the resulting establishment of a reliable polarographic method of determining carbon dioxide will require further investigation. However, if the value $x = 6$ for the coefficient of carbon dioxide in the reduction reaction corresponding to two electrons is introduced in the Ilkovic equation we get, with $n = 1/3$

$$i_d = 2.12 \times 10^3 \times C$$

That this formula is essentially correct (for $m^{2/3} \times t^{1/6} = 2.50$) we have been able to verify in a few cases. For instance, for the concentration of carbon dioxide giving $i_d = 128$ microamperes, we found $p\text{H} = 3.80$ by means of the Beckman pH meter. We then have $a_{\text{H}^+} = 1.6 \times 10^{-4}$ and[8]

$$C = a^2_{\text{H}^+}/4.31 \times 10^{-7} = 0.0594 \text{ mole per liter}$$

and $i_d = 126$ microamperes, in good agreement with the observed 128 microamperes. If the reaction had been the simpler one

$$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH$$

for instance, we would have had $n = 2$ instead of 1/3 and the current would have been six times larger. In other words, the use of the Ilkovic equation, as far as we have carried it out, verifies the result obtained from the half-wave slope, namely, that with a pair of hydrogen ions and a pair of electrons, six molecules of carbon dioxide are involved in the reduction process.

Acknowledgment.—Part of the equipment and of the materials used in this work was obtained through grants from the General Research Council of the Oregon State System of Higher Education, to which the authors express their gratitude.

Summary

1. Polarographic reduction waves obtained with solutions of carbon dioxide in 0.1 molar tetramethylammonium chloride and bromide are described.

2. The half-wave potential is 2.16 volts *vs.* the saturated calomel electrode.[11] The half-wave slope is 0.352 volt.

3. Theoretical considerations previously developed are applied to the data. It is concluded that the reduction reaction is

$$6CO_2 + H_2 \longrightarrow (CO_2)_6H_2$$

Free energy changes are calculated and discussed.

4. The influence of temperature on the half-wave potential and on the half-wave slope is reported and discussed.

5. The use of the Ilkovic equation also leads to the coefficient six for carbon dioxide in the reduction reaction.

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(11) Added in proof: After careful recalibration of the slidewire of the polarograph and the adoption of an improved method for the determination of applied potentials on the photographic records a few additional polarograms were taken. These lead us to favor the lower limit for the average half-wave potential 2.16 ± 0.03 volts.

EUGENE, OREGON RECEIVED NOVEMBER 13, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A New Magnetic Effect Applied to the Structure of Catalytically Active Solids[1]

BY P. W. SELWOOD, FRED N. HILL AND HAROLD BOARDMAN

Applications of magnetism to catalysis have recently been reviewed by the senior author.[2] The purpose of the present work was to apply magnetic susceptibility measurements to catalytically active solids such as copper–chromium oxide and related substances. It was hoped that magnetic measurements would indicate oxidation states and structural properties in these substances. During the course of the work it became evident that the magnetic suceptibility of a supported transition group oxide is described by a hitherto unrecognized principle. This principle promises to be of value in determining structure and structural changes in solid catalysts containing elements such as chromium, molybdenum, nickel and copper. The method is expected to be particularly valuable in finding the effective dispersion of the active agent in supported catalysts.

Experimental Procedures

Magnetic Measurements.—Susceptibilities were measured by the Gouy method as previously described.[3]

Preparation of Materials.—Of the approximately twenty different substances investigated, a considerable number were prepared in this Laboratory. Others were obtained elsewhere.

1. **γ-Al_2O_3.**—Samples of commercially available alumina show marked differences in magnetic susceptibilities, owing largely to differences in iron content. Susceptibilities have been found ranging from -0.3×10^{-6} to $+6.8 \times 10^{-6}$. It was found that Harshaw gamma alumina was satisfactory for the work described here. Samples of gamma alumina were also prepared in this Laboratory by the usual methods. The susceptibility found for the best samples (-0.3×10^{-6}) was independent of field strength, and almost independent of temperature.

2. **Cr_2O_3.**—C. P. chromic acid anhydride was reduced in hydrogen at 350°. The susceptibility was independent of field strength, indicating absence of ferromagnetic impurities. On the other hand, C. P. chromic oxide was, in general, unsatisfactory.

3. **Cr_2O_3-Al_2O_3 Catalyst.**—The usual method of impregnation was followed. γ-Aluminum oxide was im-

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(1) Presented at the Atlantic City Meeting of the American Chemical Society, April 10, 1946.

(2) Selwood, *Chem. Rev.*, **38**, 41 (1946).

(3) Selwood, THIS JOURNAL, **61**, 3168 (1939).

pregnated with chromic acid solution. The product was dried, then reduced in hydrogen at 350°. Several preparations averaged about 10% Cr_2O_3 as found by analysis for chromium.

4. **Cr_2O_3 Gel.**—This substance was obtained through the courtesy of Professor R. L. Burwell, Jr.[4]

5. **Ignited Cr_2O_3 Gel.**—This was the green crystalline substance, approaching chromic oxide, obtained by heating chromic oxide gel (No. 4), at 450° in hydrogen for one hour.

6. **MoO_2.**—This substance was obtained through the courtesy of Dr. B. S. Greensfelder and the Shell Development Company. It had been prepared through the reduction of C. P. molybdic anhydride in a 1:1 mole ratio of hydrogen and steam at 680–700°.

7. **MoO_2-Al_2O_3 Catalyst.**—C. P. molybdic anhydride was dissolved in ammonia water. The solution was poured over γ-alumina. The mixture was dried, then reduced in a hydrogen–steam mixture at 684°, for two hours. The catalyst so prepared contained 10% MoO_2.

8. **ZnO.**—C. P. oxide was used. This proved to be diamagnetic and to have no perceptible field strength dependence of susceptibility.

9. **ZnO-Cr_2O_3 Mechanical Mixture.**—The oxides obtained as described above were weighed out in a 1:1 mole ratio. They were thoroughly ground together in an agate mortar.

10. **ZnO·Cr_2O_3 Catalyst.**—This, and most of the other "chromite" types of catalysts listed below, were obtained through the courtesy of Professor Homer Adkins of the University of Wisconsin.[5] The catalyst was analyzed for zinc and for chromium and found to conform to a 1:1 mole ratio of oxides, within the analytical error, which was less than 0.3%. This catalyst gave only a diffuse X-ray pattern, as reported by Mr. Helmut Abt of the Physics Department of Northwestern University.

11. **$ZnCr_2O_4$ Spinel.**—The mixed oxides were calcined at 900–1000° for ten hours in an evacuated quartz tube. The product showed the characteristic spinel X-ray diffraction pattern. The patterns of unreacted zinc oxide and chromic oxide were not perceptible.

12. **$ZnCr_2O_4$ Calcined Catalyst.**—The catalyst as described above was calcined in vacuum at 900–1000° for ten hours. Both X-ray and magnetic results indicated that the product was identical with zinc chromite spinel.

13. **CuO.**—C. P. copper sulfate was treated with a very slight excess of ammonium hydroxide. The precipitate was washed, dried, and ignited at 400°. The product showed a slight field-strength dependence of susceptibility, but not enough to invalidate the results reported below.

14. **CuO-Cr_2O_3 Mechanical Mixture.**—This was prepared in a 1:1 mole ratio as described above for the corresponding zinc oxide mixture.

15. **CuO·Cr_2O_3 Catalyst.**—The preparation was one made by Dr. R. L. Sandza, formerly of this Laboratory. The preparation procedure was the familiar thermal decomposition of copper ammonium chromate. The analysis for copper and for chromium indicated an almost exact 1:1 mole ratio of CuO:Cr_2O_3.

16. **$CuCr_2O_4$ Spinel.**—The mixed oxides were calcined at 900–1000° for ten hours in vacuum. The product showed only the characteristic spinel X-ray diffraction pattern.

17. **$CuCr_2O_4$ Calcined Catalyst.**—The catalyst described above was calcined in vacuum at 900–1000° for ten hours. X-Ray evidence showed that the product was identical with copper chromite spinel.

18. **Reduced CuO·Cr_2O_3 Catalyst.**—The active catalyst (no. 15 above) was heated in hydrogen at 525° for one hour. No very pronounced change in color took place but the magnetic properties were greatly changed as shown below.

19. **NiO·Cr_2O_3 Catalyst.**—Obtained from Professor Adkins.

TABLE I

MAGNETIC SUSCEPTIBILITIES OF CATALYST SAMPLES

(The symbol, (F), indicates that the sample is ferromagnetic. In such cases the susceptibility given is the apparent susceptibility at 3950 oersteds.)

No.	Substance	Temp., °C.	Susceptibility × 10^6 This work	Other work
1	γ-Al_2O_3	25	−0.3	−0.34[a]
		−190	0	
2	Cr_2O_3	25	25.2	25.9[b]
		−190	22.8	20.1[c]
3	Cr_2O_3–Al_2O_3 catalyst	25	5.8	
		−190	19.1	
4	Cr_2O_3 gel	25	205 (F)	21[d]
		−190	905 (F)	21[d]
5	Ignited Cr_2O_3 gel	25	29.8	21[d]
		−190	153 (F)	21[d]
6	MoO_2	25	0.3	0.33[e]
		−190	0.5	
7	MoO_2–Al_2O_3 catalyst	25	0.2	
		−190	0.9	
8	ZnO	25	0	−0.3[f]
		−190	0	
9	ZnO–Cr_2O_3 mechanical mixture	25	16.5	16.4[g]
		−190	16.3	14.9[g]
10	ZnO·Cr_2O_3 catalyst	25	19.9	
		−190	41.4	
11	$ZnCr_2O_4$ spinel	25	25.8	45.0[h]
		−190	34.1	
12	$ZnCr_2O_4$ calcined catalyst	25	23.4	
		−190	33.2	
13	CuO	25	3.3	2.9[i]
		−190	1.8	
14	CuO–Cr_2O_3 mechanical mixture	25	..	17.4[g]
		−190	..	15.8[g]
15	CuO·Cr_2O_3 catalyst	25	22.4	
		−190	2000 (F)	
16	$CuCr_2O_4$ spinel	25	23.7	34.2[j]
		−190	28.5	
17	$CuCr_2O_4$ calcined catalyst	25	27.4	
		−190	45.7	
18	Reduced CuO·Cr_2O_3 catalyst	25	15.4	
		−190	27.0	
19	NiO·Cr_2O_3 catalyst	25	35.2	
		−190	110	
20	(Cu, Ba) O·Cr_2O_3 catalyst	25	20.1	
21	(Cu, Ni, Zn, Ba) O·Cr_2O_3 catalyst	25	17.9	

[a] Zimens, *Svensk Kem. Tid.*, **52**, 205 (1940). [b] Bhatnagar, *et al.*, *J. Chem. Soc.*, 1433 (1939). [c] Honda and Sone, "International Critical Tables," Vol. VI, McGraw-Hill Book Co., Inc., New York, 1929, p. 358. [d] Turkevich, *J. Chem. Phys.*, **12**, 345 (1944). [e] Wedekind and Horst, *Ber.*, **45**, 262 (1912); **48**, 105 (1915). [f] Hüttig, Radler and Kittel, *Z. Elektrochem.*, **38**, 442 (1932). [g] Additive values. [h] Hüttig, Cassirer and Strotzer, *Z. Elektrochem.*, **42**, 215 (1936); also ref. 11. [i] Klemm and Schüth, *Z. anorg. allgem. Chem.*, **203**, 104 (1931). [j] Hüttig, Kittel, *et al.*, *ibid.*, **222**, 1 (1935); **224**, 225 (1935).

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[4] Burwell and Taylor, THIS JOURNAL, **58**, 697 (1936), their preparation no. 9.

[5] Adkins, "Reactions of Hydrogen," The University of Wisconsin Press, Madison, 1937.

20. (Cu,Ba)O·Cr_2O_3 Catalyst.—Obtained from Professor Adkins.

21. (Cu,Ni,Zn,Ba)O·Cr_2O_3 Catalyst.—Obtained from Professor Adkins.

Discussion of Results

The most interesting and important of the above results are those relating to chromic oxide supported on alumina. These results will be discussed first.

For most transition group elements except the rare earth group the magnetic moment may be calculated with fair accuracy from the number of unpaired electrons in the ion, by use of the "spin-only" relationship $\mu = \sqrt{n(n + 2)}$, where μ is the moment in Bohr magnetons, and n is the number of unpaired electrons.[6] For instance, the calculated and observed magnetic moments for several elements are shown in Table II.

TABLE II

CALCULATED AND OBSERVED MOMENTS FOR SOME TRANSITION IONS

Ion	No. of unpaired electrons	Calcd. moment	Obs. moment
Cr^{+3}	3	3.87	3.8
Mn^{+2}	5	5.92	5.9
Fe^{+3}	5	5.92	5.9
Cu^{+2}	1	1.73	1.8
Mo^{+3}	3	3.87	3.7

But this excellent agreement is obtained only when the compounds investigated are magnetically dilute, that is, when the paramagnetic ions are relatively far apart. Chromic sulfate hydrate is an example of a magnetically dilute compound; chromic oxide is an example of a magnetically concentrated compound.

Magnetically dilute compounds generally follow the Curie–Weiss law, $\chi = C/(T + \Delta)$, with the constant Δ small, and the magnetic moment calculable from $\mu = 2.83 \sqrt{\chi(T + \Delta)}$. In these expressions χ is the susceptibility per mole, and T the absolute temperature.

A glance at Table I will show how far chromic oxide deviates from the Curie-Weiss law. In fact, for this compound the magnetic susceptibility is actually less at liquid air temperature than it is at room temperature. Similar large deviations from the Curie–Weiss law are found in many magnetically concentrated compounds such as oxides, sulfides and fluorides. A reason for these effects is the possible interaction of adjacent paramagnetic ions, mutually interfering with free orientation of the unpaired electron spins.[7]

Now let us compare the magnetic behavior of pure chromic oxide with that of chromic oxide supported on γ-alumina. The magnetic susceptibility of chromic oxide in such a catalyst may be calculated from the familiar Wiedemann mixture law. The results are shown in Table III. It will be observed that at liquid air temperature the susceptibility of chromium in the catalyst is over nine times larger than that of chromium in pure chromic oxide.

TABLE III

MAGNETIC PROPERTIES OF CHROMIUM IN A Cr_2O_3–Al_2O_3 CATALYST

Temp., °C.	Susceptibility of Cr_2O_3 in catalyst	Susceptibility per gram-ion of Cr^{+3}
25	62×10^{-6}	4710×10^{-6}
−190	198	15,050

From the data in Table III it is clear that the chromium in the catalyst follows the Curie–Weiss law, with the constant Δ having the modest value of 15°. We may, therefore, conclude that the interaction between chromium atoms, which occurs in the pure oxide, is effectively diminished in the catalyst. It is possible also to compute the magnetic moment of chromium in the catalyst, from the expression $\mu = 2.83 \sqrt{\chi(T + 15°)}$. The moment found is 3.4 Bohr magnetons. It must be emphasized that no such calculation is possible from magnetic measurements on the pure chromic oxide.

The magnetic moment expected for three unpaired electrons is 3.87 Bohr magnetons. It is surprising that the moment actually found for chromium in the catalyst is less than that for the Cr^{+3} ion. There is, however, no *a priori* reason why the valence of chromium in the catalyst should be identical with that in pure chromic oxide. This phase of the problem is being actively pursued in this laboratory by Mr. Robert Eischens who, in determining the susceptibility isotherms of chromia–alumina catalyst systems, finds a rapid change of the magnetic properties of chromium in the region of 10% chromium. Whatever may be the reason for this deviation from the magnetic moment expected for the +3 oxidation state, the results do not invalidate the general conclusion stated below.

It is clear from the results reported here that the magnetic behavior of chromium in the supported catalyst is like that of chromium in magnetically dilute compounds, and is in striking contrast to that of chromium in pure chromic oxide.

The effect, or principle, illustrated here for chromium on alumina may be described in this way. *The magnetic properties of a supported transition group oxide approach those of the same element at high magnetic dilution.*

This effect has been found to apply to other elements of catalytic interest, and will, presumably be applicable to all paramagnetic transition group elements. These, fortunately, are elements of major importance in catalysis.

These results confirm the view that the anomalous temperature coefficient of susceptibility shown by pure chromic oxide is not due to chromium–oxygen bonds, but is rather due to chromium–chromium interaction. The results also show that the presence of adjacent diamagnetic aluminum

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(6) Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943.

(7) Ref. 6, page 85.

ions has a negligible effect on the magnetism of the chromium ions. The supported catalyst cannot be said to contain chromic oxide in the usual sense because the chromium atoms are further apart, that is, more dispersed, than they are in pure chromic oxide. The magnetic method makes it possible to estimate the effectiveness of dispersion of a transition group element on a support. It makes it possible to follow diffusion and crystallite growth in catalysts under operating conditions, and to relate such changes to changes in catalytic activity.

A recent publication[8] indicates that chromic oxide gel has the same magnetic properties as pure crystalline chromic oxide. If this surprising result is true it means that the gel contains aggregates of adjacent chromium atoms, as in pure chromic oxide. Such a difference in the environment of the chromic ions might explain the difference in activity of the gel catalyst as compared with the supported catalyst. Unfortunately, we are unable to confirm the results reported from Princeton. We find the magnetic susceptibility of the gel to be many times larger than that of pure chromic oxide. This result was found on two separate samples. We are unable to explain the very great difference in susceptibility reported here as compared with the Princeton results. This difference is especially surprising in view of the fact that the chromic oxide gel was in both cases prepared in the same laboratory, under presumably identical conditions. The fact that our sample of the gel was strongly ferromagnetic at low temperatures may mean that very minute structural changes have a profound effect on the magnetic properties of this substance. The fact that reversion of the gel to crystalline chromic oxide gave a nearly normal susceptibility for pure chromic oxide shows that our sample could not have contained gross amounts of ferromagnetic impurities.

A further application of the magnetic method is determination of the oxidation state of the active element. This is true because change of oxidation state involves a change in the number of unpaired electrons, with consequent change of magnetic moment. The oxidation state, or combination of states, may thus be found under conditions where the X-ray, or other methods, are useless because of the near amorphous state of the catalyst.

We turn now to the molybdena–alumina catalyst. It is common experience in catalytic work that satisfactory dispersion of this element on a support is somewhat more difficult to achieve. The magnetic results confirm this experience. Molybdenum dioxide has an unusually small magnetic susceptibility,[9] whereas tetravalent molybdenum in magnetically dilute compounds has a normal moment corresponding to one unpaired electron. A catalyst containing 11% molybdenum dioxide on γ-aluminum oxide had a magnetic susceptibility only slightly larger than that of a mechanical mixture of molybdenum dioxide and γ-aluminum oxide, containing the same concentration of molybdena as the active catalyst. The supported molybdena catalyst must, therefore, contain aggregates of molybdenum dioxide, with relatively few molybdenum atoms more effectively dispersed than they are in pure crystalline molybdenum dioxide.

This result is not surprising in view of the strong tendency toward polyacid formation as we go down the sixth group of the Periodic Table. In the molybdenum catalyst the molybdenum is first adsorbed essentially in the isopolyanion form, and it remains in this geometrical arrangement throughout the drying, ignition and reduction attendant to preparation of the catalyst. If, however, effective dispersions of molybdenum on supports can be achieved by using lower concentrations, or better impregnation techniques, then the magnetic method is expected to reveal the extent of dispersion without the actual necessity of a catalytic trial.

We turn now to a discussion of the "chromite" type of catalysts. The first of these to be considered is so-called "zinc chromite." The active zinc chromite catalyst gave only a diffuse X-ray pattern. This observation does not in itself exclude the spinel structure, because unit spinel cells might be oriented at random to each other. But a zinc chromite spinel, no matter how the unit cells are oriented, would be expected to have the same magnetic properties as the crystalline spinel. But the magnetic susceptibility of the active catalyst is quite different from that of the spinel. We may conclude, therefore, that while this catalyst contains zinc oxide and chromic oxide in the proper stoichiometric proportion, it is quite definitely not a zinc chromite spinel. The magnetic evidence thus confirms a view long held by catalytic chemists. On the other hand, the active catalyst may readily be converted to a spinel by heating it for several hours in the neighborhood of 1000°. The identity of this calcined catalyst with zinc chromite spinel is established both by the X-ray diffraction pattern and by the magnetic evidence. It should also be pointed out that the active catalyst cannot be considered to be a mechanical mixture of zinc oxide and chromic oxide. Especially at low temperatures the magnetic susceptibility of the catalyst is much larger than that of the mechanical mixture. The magnetic evidence is, however, not inconsistent with the view that the catalyst is a solid solution of the two oxides. Or, we may regard the catalyst as chromic oxide supported on zinc oxide. Owing to the rather large proportion of chromic oxide present the chromic ions are not very effectively dis-

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(8) Turkevich, *J. Chem. Phys.*, **12**, 345 (1944).

(9) A possible explanation for the subnormal susceptibility of molybdenum dioxide and of related compounds lies in the increasing Mo:O radius ratio for these compounds as compared with the Cr:O radius ratio in chromic oxide. A more intimate mutual interaction may be possible in the rutile structure of molybdenum dioxide which has these metal ions in planar triangular coördination about the O^{-2} ion, than in the corundum structure adopted by chromic oxide.

persed. But the increased susceptibility at liquid-air temperatures shows that the average chromium–chromium spacing is a little larger than that in pure crystalline chromic oxide.

The same general conclusions apply to so-called "copper chromite," namely, that the active black catalyst is not a spinel. This is established through the absence of characteristic X-ray diffraction and by the very different magnetic properties. This catalyst is, however, characterized by a very remarkable ferromagnetism which is found at liquid air temperatures. The Curie temperature for this substance lies between liquid air temperature and room temperature because not a trace of ferromagnetism is observable at 25°. Further work is in progress to find the exact Curie point. This ferromagnetism is not found in the adequately calcined catalyst, although prolonged heating is necessary to make the catalyst revert completely to copper chromite spinel. The ferromagnetism of this catalyst recalls that found for the chromic oxide gel. It is not clear that there is necessarily any relationship between the ferromagnetism and the catalytic activity. But the existence of ferromagnetism must be remarkably sensitive to rather minor changes in structure, and it is possible that such structural changes do have a relationship to catalytic activity.

It is well known that the copper oxide–chromium oxide black catalyst undergoes a change when it is heated in hydrogen. The black form is believed to contain divalent copper, while the reduced form contains either univalent copper or copper metal.[5] The reduced form was found in these experiments to show no trace of ferromagnetism. In fact the susceptibility dropped to a value not greatly different from that for the corresponding active zinc catalyst. Zinc ions are, of course, diamagnetic, as are both cuprous ions and copper atoms. The magnetic evidence is, therefore, not inconsistent with the view that the reduced catalyst contains cuprous ions or metallic copper, together with a rather slightly dispersed form of chromic oxide.

The magnetic results on the nickel–chromium oxide are a little surprising as it was thought, by analogy, that this catalyst would also be ferromagnetic at low temperatures. The absence of any ferromagnetism also implies the absence of metallic nickel. This is not unexpected, although nickel-containing catalysts not infrequently give magnetic evidence of some metallic nickel, even though the presence of metal would not have been predicted on consideration of the previous treatment of the catalyst. Further study of this catalyst may throw some light on the problem as to whether reduced copper–chromium oxide contains metallic copper or cuprous ions.

It is a pleasure to acknowledge a grant-in-aid of research from the Shell Development Company. The investigation was also supported by a grant from the Abbott Fund of Northwestern University.

Summary

Magnetic susceptibility measurements have been made on catalytically active solids consisting of chromic oxide supported on γ-alumina, on molybdenum dioxide supported on γ-alumina, and on a group of so-called "chromite" catalysts. It has been shown that the magnetic properties of a supported transition group oxide approach those of a magnetically dilute compound. This effect is expected to be useful in studying the structure of active solids, in estimations of dispersion and of surface area, and of the oxidation state of the activating agent.

EVANSTON, ILLINOIS RECEIVED JUNE 10, 1946

[CONTRIBUTION FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Regulator Theory in Emulsion Polymerization.[1] I. Chain Transfer of Low Molecular Weight Mercaptans in Emulsion and Oil-Phase

BY W. V. SMITH

In a general consideration of the mechanism of vinyl polymerization, Flory[1a] suggested that growing polymer free radicals might react with solvent molecules, producing inactive polymer molecules and solvent free radicals; and that this transfer reaction might explain the effectiveness of some solvents in reducing the molecular weights of polymer produced in them. More recently, Mayo[2] has discussed this idea quantitatively and has interpreted the molecular weights of polystyrene produced in various solvents in terms of the ratios of the rate constants for chain growth and chain transfer with the solvent. Early in the current synthetic rubber program it was proposed that the effectiveness of mercaptans in improving the processing characteristics of GR-S was due to their ability to reduce or "regulate" the molecular weight of the polymer produced in their presence; since it was found that mercaptan would reduce the molecular weight of emulsion polystyrene.[3] It was then shown that the

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(1) These papers, Parts I, II and III, were presented at the High Polymer Forum of the Chicago meeting of the American Chemical Society, Sept., 1946.

(1a) P. J. Flory, THIS JOURNAL, **59**, 241 (1937).

(2) F. R. Mayo, *ibid.*, **65**, 2324 (1943).

(3) R. H. Ewart, private communication.