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THE RELATIONSHIP BETWEEN THE MAGNETIC MOMENT OF A METAL ATOM AND ITS CATALYTIC ACTIVITY.

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It has been often noticed that the catalytic activity of substances has some relationship with their magnetism. The most typical examples are given in some homogeneous ortho-para-hydrogen conversion.[1] The interconversion of hydrogen is catalyzed by the oxygen molecule,[2] whose catalytic activity is in practice due to its magnetic moment in the ground state ($^3\sum$). Such molecules as NO, NO_2, or many free radicals, which are paramagnetic, can also bring forth the transformation. In solutions the paramagnetic ions of the ferrous iron or rare earth metals[3] have also the ability for this conversion. In these cases it is shown that the conversion takes place by the influence of the non-homogeneous magnetic field in the neighbourhood of the paramagnetic molecules or ions.[4]

In heterogeneous reactions, though it is generally recognized that the ferromagneticor strongly paramagnetic substances possess high catalytic activities,[5] the general argument concerning the relationship between the activities of many catalysts and their magnetism is so far insufficiently presented. Taylor and Diamond[6] have shown in their experiment on the ortho-para-hydrogen conversion on the surfaces of various catalysts at low temperatures that the transformation took place efficiently on the surfaces of the catalysts with large magnetic susceptibilities, but also this conversion occurred even on the surfaces of the catalysts diamagnetic in bulk such as silver.

A heterogeneous catalytic reaction is believed, in general, to take place on the active centers of the surface of a catalyst,[7,8] and as those atoms on such

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[1] A. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen," 1935.

[2] L. Farkas and H. Sachsse, Z. physik. Chem., B 23, 1 (1933).

[3] L. Farkas and H. Sachsse, Z. physik. Chem., B 23, 19 (1933); H. Sachsse, ibid., B 24, 429 (1934).

[4] E. Wigner, Z. physik. Chem., B 23, 28 (1933).

[5] M. Kröger, "Grenzflächen-Katalyse," 1933; K. Fischbeck and F. Salzer, Z. Elektrochem., 41, 158 (1935); J. A. Hedvall and others, ibid., 41, 445 (1935); Z. physik. Chem., B 27, 196 (1934); ibid., B 29, 455 (1935); ibid., B 30, 280 (1935); H. S. Taylor and A. Sherman, Trans. Farad. Soc., 28, 247 (1932); J. Amer. Chem. Soc., 53, 1614 (1931); Y. Urushibara and M. Takebayashi, Bull. Chem. Soc. Jap., 11, 692, 754 (1936); ibid., 12, 51, 138 (1937); etc.

[6] H. S. Taylor and H. Diamond, J. Amer, Chem. Soc., 57, 1251 (1935); ibid., 55, 2613 (1933).

[7] J. W. McBain, "The Sorption of Gases and Vapours by Solids," 1932; S. J. Gregg, "The Adsorption of Gases by Solids," 1934; H. S. Taylor, Z. Elektrochem., 35, 542 (1929).

[8] H. S. Taylor, Proc. Roy. Soc., A 108, 105 (1925); J. Phys. Chem., 30, 145 (1926).

centers actually take part in the mechanism of the catalytic reaction, it is desirable to see whether the character of the atoms on the catalyst surface is correlated to its catalytic activity[9] or not. Though the character of the atom in the interior of the space lattice of a metal crystal may differ considerably from that of the isolated atom in the gaseous state, the character of the surface atom or the atom on the edge, corner, or point of the crystal, namely on the so-called active centers, will approach more and more to that of the gaseous atom.[8] It is assumed here that the character of the atom on the active center may approximately be given by the data of an isolated atom in the gaseous state.

As the activity of a catalyst may be, to some extent, due to the chemical valency force of the surface atoms, and as the free valency is always attended by magnetic moments as seen in free radicals, there may generally exist an intimate relationship between the magnetism of the atom on the active center of a catalyst and its catalytic activity.

The magnetic moment of the atom in the gaseous state can be calculated from the spectroscopic data.[10] In formula (1) the magnetic moment μ is expressed by the inner qnantum number J and the Landé g-factor;

$$\mu=\sqrt{J(J+1)}\, g\, \mu_0, \qquad (1)$$

where μ_0 is the Bohr magneton ($\mu_0=eh/4\pi mc$). The Landé g-factor is obtained from the formula;

$$g=1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}. \qquad (2)$$

Table 1 gives the list of elements with the magnetic moments of their atoms in the ground state[10] at the temperature of absolute zero; all the elements in Part I are transition elements and those in Part II are the others; and the magnetic moment is expressed in the Bohr magneton unit.

It is apparent from Table 1 that the metals which are frequently used as active catalysts in various catalytic reactions possess large magnetic moments of their atoms; while those of poor catalytic activity have usually small or zero magnetic moments. In Part I, however, some metals are found which have small magnetic moments in spite of their high catalytic activities. These atoms possess generally large magnetic moments in the multiplet levels for the lowest electro-

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9) Though activities of various catalysts cannot be quantitatively measured, there is no doubt that there exist differences of catalytic activities in metals.

10) W. Klemm, "Magnetochemie," 1936; G. Herzberg, "Atomspektren und Atomstruktur," 1936.

Table 1.*)

Magnetic moments of atoms in ground states.

Atom	Symbol	L	S	J	g-Factor	Magnetic moment in Bohr's magneton unit
Part I.						
Ru.	$^5F_5$	3	2	5	7/5	7.67
Cr, Mo.	$^7S_3$	0	3	3	2	6.93
Fe, (Os).	$^5D_4$	2	2	4	3/2	6.70
Co, Rh, (Ir).	$^4F_{9/2}$	3	3/2	9/2	4/3	6.63
Mn.	$^6S_{5/2}$	0	5/2	5/2	2	5.92
Ni, (Pt).	$^3F_4$	3	1	4	5/4	5.59
Pt.	$^3D_3$	2	1	3	4/3	4.62
Nb.	$^6D_{1/2}$	2	5/2	1/2	10/3	2.88
Ti, Zr, (Hf).	$^3F_2$	3	1	2	2/3	1.63
Sc, Y, (La).	$^2D_{3/2}$	2	1/2	3/2	4/5	1.55
V, (Ta).	$^4F_{3/2}$	3	3/2	3/2	2/5	0.77
W.	$^5D_0$	2	2	0	—	0.00
Pd.	$^1S_0$	0	0	0	—	0.00
Part II.						
N, P, As, Sb, Bi.	$^4S_{3/2}$	0	3/2	3/2	2	3.88
O, S, Se, Te, Po.	$^3P_2$	1	1	2	3/2	3.68
F, Cl, Br, I.	$^2P_{3/2}$	1	1/2	3/2	4/3	2.58
H.	$^2S_{1/2}$	0	1/2	1/2	2	1.73
Li, Na, K, Rb, Cs.	$^2S_{1/2}$	0	1/2	1/2	2	1.73
Cu, Ag, Au.	$^2S_{1/2}$	0	1/2	1/2	2	1.73
B, Al, Ga, In, Tl.	$^2P_{1/2}$	1	1/2	1/2	2/3	0.58
C, Si, Ge, Sn, Pb.	$^3P_0$	1	1	0	—	0.00
Be, Mg, Ca, Sr, Ba.	$^1S_0$	0	0	0	—	0.00
Zn, Cd, Hg.	$^1S_0$	0	0	0	—	0.00
He, Ne, Ar, Kr, X.	$^1S_0$	0	0	0	—	0.00

*) Table 1 does not contain the rare earth elements in Part I, but some of them possess remarkably large magnetic moments.

nic states or in other electronic excited states, whose energy differences from the ground states are so small that the atoms may easily be raised to those of excited states by the thermal energy. For example, the atomic states of tungsten, vanadium, and titanium have the term values as shown in Table 2.[11] If the energy of about 8 kcal is given to the tungsten atom, it is excited to the $^7S_3$ state. With only about 2 kcal the vanadium atom is excited to the $^4F_{9/2}$ state, and with about 7 kcal to the $^6D_{9/2}$ state. With only about 1 kcal the titanium atom is excited to the $^3F_4$ state. These excited states possess large magnetic moments as shown in Table 2, and the atoms in these states will be catalytically active. The elements

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[11] R. F. Bacher and S. Goudsmit, "Atomic Energy States," 1932.

in Part II of Table 1, on the contrary, possess no large magnetic moments in easily attainable low energy levels. In general, it is the characteristic feature of the elements in Part I that their atoms have many higher excited states with large magnetic moments or large J values,[11] while the atoms of the elements in Part II have relatively small J values in the excited states with the exception of the copper[12] atom.

Table 2.

Term values of excited states of atoms and their magnetic moments.

Atom	Configuration	Symbol	J	Term value (cm^{-1})	Excitation energy (kcal)	g-Factor	Magnetic moment (μ_0)
W	$5d^4\,6s^2$	^5D	0	0.00	0.0	—	0.00
			1	1670.27	4.7	$3/2$	2.12
			2	3325.50	9.5	$3/2$	3.68
			3	4829.99	13.7	$3/2$	5.19
			4	6219.30	17.6	$3/2$	6.71
	$5d^5\,6s$	^7S	3	2951.27	8.4	2	6.93
V	$3d^3\,4s^2$	^4F	$3/2$	0.00	0.0	$2/5$	0.78
			$5/2$	137.38	0.4	$36/35$	3.04
			$7/2$	323.42	0.9	$26/21$	4.92
			$9/2$	553.02	1.6	$4/3$	6.63
	$3d^4\,4s$	^6D	$1/2$	2112.32	6.0	$10/3$	2.88
			$3/2$	2153.20	6.1	$28/15$	3.62
			$5/2$	2220.13	6.3	$58/35$	4.90
			$7/2$	2311.37	6.5	$100/63$	6.30
			$9/2$	2424.89	6.9	$14/9$	7.73
Ti	$3d^2\,4s^2$	^3F	2	0.00	0.0	$2/3$	1.63
			3	170.14	0.5	$13/12$	3.75
			4	386.88	1.1	$5/4$	5.59
	$3d^3\,4s$	^5F	1	6556.86	18.6	0	0.00
			2	6598.83	18.7	1	2.45
			3	6661.00	18.9	$5/4$	4.33
			4	6742.79	19.1	$27/20$	6.04
			5	6843.00	19.4	$7/5$	7.67

It becomes clear that the catalytic activity of metals is in a close connection with the magnetic moment of their atoms. The magnetic susceptibility, which has been frequently correlated to the activity of catalysts, is a macroscopic property of substances[13] and detectable only in a magnetic field; while the magnetic moment of an atom is a microscopic property permanently possessed by the individual atoms, and is indifferent to the existence of an external

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12) Also copper is used as the active catalyst in many cases; see, for example, R. H. Griffith, "The Mechanism of Contact Catalysis," 1936.

13) For the theories of the magnetic susceptibility: P. Langevin, Ann. Chim. Phys., (8) 5, 70 (1905); P. Weiss, Physik. Z., 9, 358 (1908); W. Heisenberg, Z. Physik, 49, 619 (1928); W. Pauli, Z. Physik, 41, 81 (1927); J. H. van Vleck, "The Theory of Electric and Magnetic Susceptibilities," 1932.

magnetic field. Any relationship, therefore, between the magnetic susceptibility of metals and their catalytic activities will not be concerned directly in the mechanism of catalytic reactions. It is the atomic property of the metal rather than its bulk property, which is concerned directly in the mechanism of catalysis, and this seems to fit the experimental facts. While the magnetic susceptibility of ferromagnetic metals is enormously large as compared with that of strongly paramagnetic metals,[14] the magnetic moment of the atom of the former is approximately of the same magnitude in comparison with that of the latter (Tables 1 and 2). Also in some diamagnetic metals the magnetic moment of their atoms is not always zero, and the result obtained by Taylor and Diamond[15] becomes fairly explainable in this light.[16] Consequently, the above-mentioned relationship between the magnetic moment of the atom of metals and their catalytic activities may give an account of the nature of the catalytic activity.

It becomes evident that what is intimately correlated to the mechanism of catalysis is the microscopic character of the atoms on the active centers of a catalyst rather than the macroscopic character of its whole crystal. It follows then thatone of the causes of catalytic action of a metal catalyst, in general, might be the influence of the localized non-homogeneous magnetic field on its surface produced by the permanent magnetic moments of the metal atoms probably situated on the active centers of the surface. The interaction between the non-homogeneous magnetic field in the vicinity of the active centers and the magnetic moments of the gaseous particles taking part in the reaction should also be considered in order to explain the specific nature of the catalytic reaction. It will be interesting to investigate experimentally the action of an extremely non-homogeneous magnetic field produced artificially in place of that of a natural catalyst.

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14) The magnetic susceptibility per gram atom of the ferromagnetic metals (Fe, Co and Ni) is of the order of 10^5-10^2, while that of paramagnetic metals is of the order of $10^{-4}-10^{-5}$ at ordinary temperatures, for example, Mn(490×10^{-6}), Pt(156×10^{-6}), Cr(150×10^{-6}), V(76×10^{-6}) and W(41×10^{-6}). Though the ratio of the magnetic susceptibilities of the two classes of metals is incomparably large, the activities of their catalysts do not correspond to it.

15) loc. cit.

16) Though silver is a diamagnetic metal in bulk (magnetic susceptibility: -22×10^{-6}), the silver atom has a magnetic moment (Table 1).