JOURNAL OF CATALYSIS 3, 105-106 (1964)

NOTE

A Relationship between the Energy Levels of Ions and the Polarization Fraction

Received August 14, 1963

We wish to report some preliminary results in the establishment of a quantitative relationship between the "polarization fraction" and fundamental properties of metal ions.

The proposal that intermedions are bonded to some type of delocalized orbital is consistent with the description of chemisorption presented in previous papers (*1–3*) as well as with the identification of intermedions as strongly polarized but weakly bonded adsorbates. For example, copper has a polarization fraction of 0.32. The "surface orbital" changes the vibration frequency of adsorbates from that of the gas to frequencies which correspond to nonintegral numbers of valence electrons having different integers but a constant fraction of 0.32. It has been proposed (*3*) that the surface copper ions responsible for the formation of intermedions may be represented by electronic configurations of $3d^{8.32}$ and $3d^{9.32}$ instead of the conventional $3d^9$ and $3d^{10}$. On this basis, the polarization fraction might arise as the resultant of the contributions of low-lying energy levels to the actual electronic configuration of the metal ion.

The energy levels of atoms and ions are determined from analyses of optical spectra. The contribution of the levels above the ground state to the configuration of the atom or ion is proportional to the probability of finding electrons in these levels. This in turn is proportional to the sum of the Maxwell-Boltzman factors times the respective multiplicities. Table 1 presents the sums of energy levels calculated from values of J and $\bar{\nu}$ from the "Atomic Energy Level" tables (*4*) for the energy states *above* the ground state for ions of metals whose polarization fractions are known. With the replacement of E by $hc\bar{\nu}$, the weighting factor becomes:

$$(2J+1)\ \exp -(hc\bar{\nu}/kT) = (2J+1)\ \exp -(1.44\bar{\nu}/T)$$

Also included in Table 1, are the polarization fractions of the metals determined from carbon monoxide chemisorption and from known catalytic reactions by the methods described in the preceding paper. Figure 1 is a semilog plot of the data of Table 1. The metal atoms (state I) have not been included, since, in all cases of CO chemisorption the metals are in a state different from that of the isolated atom. The Roman numerals correspond to the ionization states in accordance with spectroscopic notation.

The ions considered are the first two which have low-lying energy levels. For example, Cr(I) is excluded since it is the atom; for Cr(II) the first state above the ground state will not make a contribution below approximately 1800°K; Cr(III) and Cr(IV) have levels which are available at

TABLE 1

SUM OF ENERGY LEVELS ABOVE GROUND STATE AT 298°K AND POLARIZATION FRACTION

Metal	Polarization fraction	Ion	Configuration	$(2J+1)\exp(-hc\bar{\nu}/kT)$
Chromium	0.099	Cr(III)	$3d^4$	6.11
		Cr(IV)	$3d^3$	2.46
Iron	0.257	Fe(II)	$3d^64s$	1.55
		Fe(III)	$3d^6$	1.02
Cobalt	0.633	Co(II)	$3d^8$	0.072
		Co(III)	$3d^7$	0.141
Nickel	0.857	Ni(II)	$3d^9$	0.0028
		Ni(III)	$3d^8$	0.0098

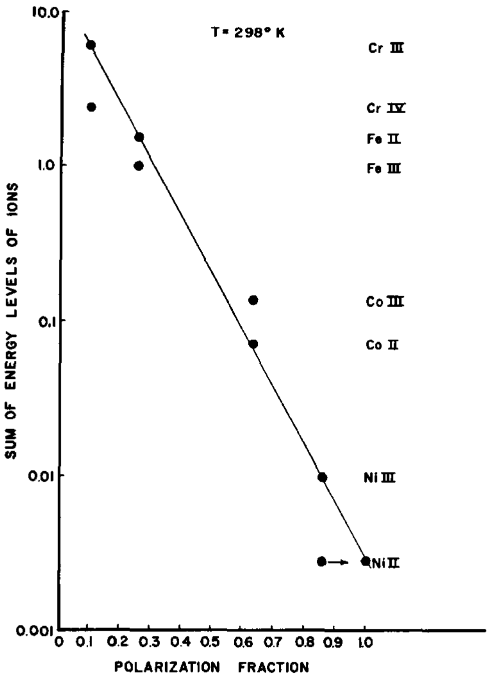

FIG. 1. Energy levels from optical spectra and polarization fractions from CO chemisorption.

moderate temperatures. In Fig. 1 it is observed that a straight line passes through one of the ions of each metal, viz., Cr(III), Fe(II), Co(II), and Ni(III). This relationship between these quantities persists up to 500°C for these metal ions.

The significance of the sums of energy levels for the other ions of each of the metals is suggested by an interpretation of data published by Pickering and Eckstrom (*5*) from their study of the chemisorption of CO on vacuum-evaporated nickel films. In addition to infrared bands which correspond to gaseous CO (2170 and 2122 cm^{-1}) and to the CO intermedion with 10.85 valence electrons (2058.0 cm^{-1}), they observed an infrared absorption band at 2030.0 cm^{-1}. This band was readily removed by evacuation. According to the equation relating vibration frequency and number of valence electrons for CO species (*2*), this frequency corresponds to a CO intermedion having 11.00 valence electrons. A sum of energy levels of 0.0028 with a polarization fraction of 1.00 for Ni(II) agrees quite well with the other points on the line in Fig. 1. This illustrates the obvious conclusion that the polarization fractions of the different ions of each metal must be different. Perhaps the ions which define the straight line in Fig. 1 are the most common states for these metals. On the basis of this line, if these other ionization states were detected by chemisorption, they would have polarization fractions of: Cr(IV), 0.205; Fe(III), 0.308; and Co(III), 0.543. Further experimentation will be necessary to test this proposal.

The foregoing observation presents a relationship between the atomic energy levels and the polarization fraction that appears to be unexpectedly simple. Since the preceding publication (*3*) provides a relationship between the polarization fraction and chemisorption and catalysis, this observation seems to provide a fundamental basis for the hypotheses and concepts of this theory of catalysis. While this relationship between the energy levels of the ions and the polarization fraction has been observed, it remains to be explained and tested for many other metals.

ACKNOWLEDGMENT

The authors wish to thank The Standard Oil Company (Ohio) for permission to publish this work.

REFERENCES

1. GARDNER, R. A., AND PETRUCCI, R. H., *J. Am. Chem. Soc.* **82**, 5051 (1960).
2. GARDNER, R. A., AND PETRUCCI, R. H., *J. Phys. Chem.* **67**, 1376 (1963).
3. GARDNER, R. A., *J. Catalysis* **3**, 7–21 (1964).
4. MOORE, C. E., "Atomic Energy Levels," Vol. II. *Natl. Bur. Standards Circular* **467** (1952).
5. PICKERING, H. L., AND ECKSTROM, H. C., *J. Phys. Chem.* **63**, 512 (1959).

R. A. GARDNER
T. B. SELOVER, JR.

The Standard Oil Company (Ohio)
Research Department
Cleveland, Ohio