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MassSpectrometric Study of the OsmiumOxygen System

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velocities, even though the pressure pickup was at the near position. This concord between the pressure measured at the 6-in. position and the far-position reflected-shock speed indicates that the wave, as it passed the SLM pickup, was traveling at a speed near this average value. This would mean that the pressure, as well as the shock speed, depends upon the location selected to make the measurement. The departures of measured P_{51}'s from the ideal, when translated to temperature, were averaged for M_s ranges 2.5–3.0 and 3.0–3.5 and amounted to about 40° and 60°K respectively, just as Skinner concluded.

Following the initial pressure jump, the traces show a continued slow rise, such as Skinner described. At 500 μsec after the jump, many of the traces indicated a pressure slightly larger than that expected for an ideal reflection.

In conclusion, it appears that the values of both M_{rs} and p_5 depend upon the position selected to record the measurement. It is believed that reaction temperatures derived from pressure measurements are better than those from M_{rs} measurements, because the pressure reflects the time-temperature history over the region in question.

[1] R. A. Strehlow and A. Cohen, J. Chem. Phys. **30**, 257 (1959).

[2] G. B. Skinner, J. Chem. Phys. **31**, 268 (1959).

[3] Made by us, using Clevite Corporation's PZT-5 crystal elements.

[4] Purchased from Kistler Instrument Company, Model No. 680.

[5] Herman Mark, "The interaction of a reflected shock wave with the boundary layer in a shock tube," NACA TM 1418 (1958).

Quantum-Mechanical Approximations to Chemical Systems*

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THE observables, the atomic diamagnetic susceptibilities of rare gases (I), χ_A, can be used to obtain average square radial distribution functions.[1] Using Slater's orbitals (II), the appropriate screening parameters s and the "principal" quantum numbers n^* can be calculated.[1] In this way, reasonably precise "theoretical" values of χ_A can be obtained for isoelectric ions. For (II), no distinction is made between s and p atomic orbitals.

$$\chi_A = (-e^2N/6mc^2)\sum_{n^*}\langle r^2\rangle_{\text{Av }n^*}, \tag{I}$$

$$\langle r^2\rangle_{\text{Av }n^*} = [n^{*2}(n^*+\tfrac{1}{2})(n^*+1)]/(Z-s)^2. \tag{II}$$

We have applied the conditions of (1) similar screening parameters and (2) no distinction between s and p electrons to the calculation of the molecular susceptibility of ethylene. Condition (1) is quite easily met, but condition (2) requires that the description of the electrons for the carbon-carbon bond must not be the usual $\sigma(sp^2)$ and π atomic orbitals but must be, for example, two equivalent sp^3 atomic orbitals inclined at one-half the tetrahedral angle from a line joining the carbon atoms and in a plane perpendicular to the molecular plane—the "bent-bond" structure for ethylene.[2] Using such orbitals and the variation method of Guy and Tilleiu[3] for the calculation of molecular susceptibilities, we have determined the theoretical value for the diamagnetic susceptibility of ethylene, χ_M, to be -20.48×10^{-6}. This would yield better agreement with the experimental values for ethylene-type molecules.[3]

There appears to be some arbitrariness as to which function is more appropriate in the description of the properties of a substance as ethylene. The σ–π structure would seen more appropriate in the description of the ultraviolet spectra of ethylene, while the "bent-bond equivalent orbital (EO)" approach seems preferable in this instance.

But is there indeed a question of arbitrariness? We believe not. We suggest that both representations are correct and for frequencies associated with electronic excitation the molecule appears to have an electron distribution approximated by σ–π, but over the longer time of molecular vibration-rotation the EO description more exactly represents the electron distribution.

Thus it is suggested that a "resonance" description of ethylene is required, as part of the zero-point character of the molecule, with the σ–π electron orbital description appropriate for high frequency experiments and the EO for lower frequencies, i.e., for most "chemically" important phenomena. An extension to similar chemical systems can be made.

* Support by a grant from the Research Corporation is gratefully acknowledged.

[1] J. C. Slater, Phys. Rev. **32**, 349 (1928); **38**, 57 (1930).

[2] J. A. Pople, Quart. Rev. **11**, 273 (1957).

[3] J. Guy and J. Tillieu, Compt. rend. **242**, 1279 (1956); J. Chem. Phys. **24**, 1117 (1956).

Mass-Spectrometric Study of the Osmium-Oxygen System*

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WITH the exception of the osmium and ruthenium tetroxides, the existence of platinum metal oxides in the vapor phase has been a matter of conjecture.[1] In addition, reliable thermodynamic data for either the solid or gaseous platinum metal oxides are virtually nonexistent. Based on the limited information available, Brewer[1] has predicted that, at temperatures in excess of 1500°K and 1 atm oxygen, the M_xO and

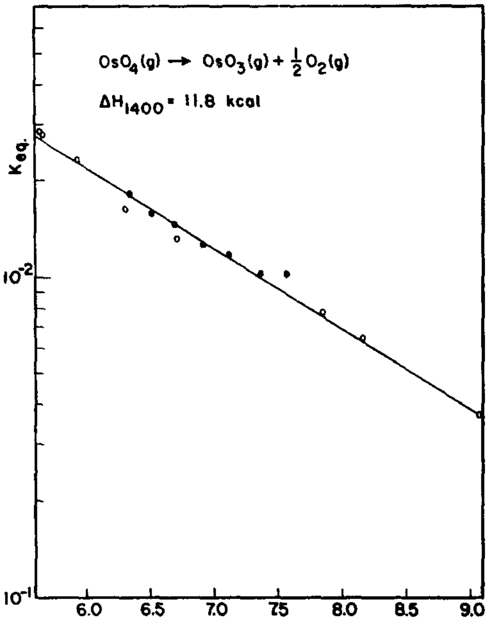

FIG. 1. Equilibrium constant, $K=P_{OsO_3}P_{O_2}^{\frac{1}{2}}/P_{OsO_4}$ (pressures in atmospheres) as a function of $1/T\times10^{4}$°K^{-1}.

M_xO_2 gaseous suboxides would be the only important species in the osmium-oxygen system. This paper presents the results of a study of the osmium-oxygen system.

The mass spectrometer and associated experimental techniques have previously been described,[2] with the exception that a gas-inlet system was added to permit admission of oxygen within the Knudsen cell at controlled pressures. The internal liner of the cell, which contained the sample of finely powdered Johnson, Matthey spectroscopic osmium, was made of Morganite alumina,[3] while the cell itself was fabricated from molybdenum.

In the temperature range 1100–1750°K, the main ionic species produced from the vapor effusing from the Knudsen cell were OsO_3^+ and OsO_4^+ with approximate appearance potentials of 12.3±1 and 12.6±1 ev. The ion-intensity ratio of OsO_3^+ to OsO_4^+ was a function of the oxygen pressure and the temperature, thus confirming the presence of at least two stable osmium oxide molecules in the vapor phase. Taking into account the appearance potentials, we ascribe these ions to simple ionization of OsO_3 and OsO_4.

At higher temperatures (>1700°K) there is evidence to support the existence of a stable OsO_2 molecule. The intensity of the OsO_2 species is $\leq 1/1000$ of the OsO_3 intensity. Under the conditions of this study, no other lower oxide species, as suggested by Brewer, could be detected.

A plot of the equilibrium constants vs $1/T$ for the reaction $OsO_4(g) \rightarrow OsO_3(g) + \frac{1}{2}O_2(g)$ is given in Fig. 1. The circles represent values determined at an average oxygen pressure of 3.5×10^{-5} atm, whereas the solid data points were taken at an average oxygen pressure of 1.2×10^{-5} atm. The invariance of the equilibrium constant over a threefold change in oxygen pressure would tend to indicate that equilibrium had been established in the gas phase reaction. The $\Delta H_T°$ ($T=1400$°K) for the reaction was found to be 11.8±1 kcal/mole.

A more complete study of the platinum metals-oxygen systems will appear in forthcoming publications.

* Supported in part by the Office of Ordnance Research, U. S. Army, and in part by the National Science Foundation.

[1] L. Brewer, Chem. Revs. **52**, 1 (1953).

[2] M. G. Inghram and J. Drowart, "Mass spectroscopy applied to high temperature chemistry," appearing in *Proceedings of an International Symposium on High Temperature Technology at Asilomar, California* (McGraw-Hill Book Company, Inc., New York, 1959), p. 219ff.

[3] Morganite Incorporated, Long Island City, New York.

Some Remarks on the Electron Affinity of Atomic Lithium*

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An earlier report quoted an roughly made approximation of the electron affinity of atomic lithium.[1] So far, this quantity has not been measured in the laboratory. Unfortunately, the method of photodetachment does not appear to be as applicable to Li^- as to many of the heavier negative ions.[2]

From a theoretical point of view, however, it is possible to compute the affinity with a precision limited by the extremely hard numerical work.

In Lithuania, Jucys *et al.* have recently computed $EA(\mathrm{Li})=0.462$ ev when using Hartree-Fock solutions in a three-configurational approximation with amending configurations $1s^22p^2$ and $2s^22p^2$.[3] The purpose of this note is to reinvestigate the semiempirical computations and consider the results in light of this new theoretical value.[4]

The extrapolations may be expressed explicitly as

$$J_n(Z)=\sum_{k=1}^{n+1}(-1)^{k+1}\binom{n+1}{k}(1+kZ^{-1})^{n-2}J(Z+k), \qquad (1)$$

provided $n\geq2$.

In this way, the physically significant series

$$J_n(Z)=\sum_{j=0}^{n}c_jZ^{2-j}$$

is used as extrapolation formulas starting with the quadratic extrapolation when $n=2$.[5] It should be noted that the values of $J(Z+k)$ are the observed ionization potentials of the members of the sequence isoelectronic with $Li^-(Z=3)$. Recent revisions of the spectroscopic data of the helium sequence show that the figures given by Moore for the beryllium sequence are by no means all significant.[6] It has therefore been