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North Carolina University

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First Annual Technical Report

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Relating work performed from 1 June 1973 to 31 May 1974

on projects as follows:

1. Application of Machine Decisions to Failure Analysis
   T. L. Isenhour

2. Homogeneous Catalysis of Net Electrochemical Reactions as Applied to Fuel Cells
   T. J. Meyer

3. Failure of Inhomogeneous Rocks under Static Loads
   D. E. Dunn

4. Theoretical Investigation of Solid Electrolytes
   S. Choi

5. Fine Powder Technology of Reactive Metals
   R. D. Rieke

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13. ABSTRACT

This report recounts the results in the first year's work on the topics and by authors as follows:

1. Application of Machine Decisions to Failure Analysis
   Thomas L. Isenhour
2. Homogeneous Catalysis of Net Electrochemical Reactions as Applied to Fuel Cells
   Thomas J. Meyer
3. Failure of Inhomogeneous Rocks under Static Loads
   David E. Dunn
4. Theoretical Investigation of Solid Electrolytes
   Sang-il Choi
5. Fine Powder Technology of Reactive Metals
   Reuben D. Rieke

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Summary of Research Activities:

(1) Theoretical Study of Ionic Transport in Solid Electrolytes - β-Alumina

In order to understand the dynamics of carrier ions (mobile cations) in β-alumina, we have calculated the potential energy curves for correlated motions of these ions.

Since the x-ray and neutron diffraction studies of Na and Ag β-alumina show that these ions move on a two-dimensional network of hexagons, we restrict the motion of carrier ions to the lines of this network.

Our calculation shows two sets of alternating vertices. (See Fig. I) One set we have designated as Site 1 vertices; these coincide with the one particle potential energy minima. The other, Site 2 vertices, do not correspond to the potential minima.

In order to calculate the potential energy surface we consider (1) Coulomb potential due to point charges, (2) Born-Mayer repulsive potential between ions, and (3) the polarization energy. The polarization energy is calculated in a self-consistent manner.

Calculations have been done for various carrier ions (i.e. Li, Na, K, Ag, Rb) with the assumption that the crystal parameters remain unchanged.

The composition of the crystal with all Sites 1 filled with carrier ions (M^+) corresponds to $M_2O \cdot 11\ Al_2O_3$ which we may call the "ideal structure." In this structure the potential energy of Site 2 is higher than that of Site 1 by more than 2 eV for all carrier ions considered. β-alumina samples reported in the literature have excess M^+ ions and charge neutrality is maintained either by extra oxygen ions or by vacancies of aluminum ions, or bivalent ions substituted for aluminum ions.

In the "ideal structure" the barrier height for the motion of a carrier ion is expected to be an order of magnitude larger than the experimentally measured values of the activation energy for diffusion and electrical conduction. This suggests some kind of correlated motion of carrier ions in the presence of M^+ ions in excess of the ideal structure. As the initial configuration of ions in our model, an extra M^+ ion is placed at a Site 2 in the ideal structure. As the ion at a Site 1 is moved toward an empty Site 2, the M^+ ion at the nearest Site 2 moves in. (See Fig. 2) Potential energy values are calculated as the first ion is moved and the position of the second ion (started at Site 2) is adjusted to minimize the total potential energy of the system. This calculation is done at intervals 0.16 Å until the first ion reaches the originally empty Site 2. From this calculation one can see that the minimum potential energy corresponds to the two M^+ ions located between two different sites (i.e. between the lattice vertices). The potential energy difference between the maximum and the minimum may be interpreted as the activation energy in this correlated motion of the pair.

To improve the calculation we considered the correlated motion of six M^+ ions. The initial configuration is identical to that of the previous calculation. As one M^+ at Site 1 is moved toward an empty Site 2, the positions of the M^+ ion at the nearest Site 2 and four M^+ ions at nearby Site 1 are allowed to adjust to minimize the potential energy of the system. (See Fig. 3) The potential energy values as a function of the displacement of the M^+ (originally at Site 2) are given in Fig. 4. Again one notices that the potential energy minima correspond to the location of two ions in between adjacent vertices of a hexagon. A very interesting result of this calculation is that other four M^+ ions do not move away from their original positions (Sites 1), but each remains near its original location (Site 1) with small displacements as shown in Fig. 3 while two M^+ ions move the length of one side of a hexagon. The energy difference between the maximum and minimum positions may be interpreted as the activation energy and these values are listed in Table I and compared with reported activation energies of electrical conduction. The agreement seems to be satisfactory except for Li^+. The

disagreement on Li^+ is not surprising since Li^+ ion is not expected to move along the sides of hexagons. (A separate numerical computation of a one particle potential energy curve along lines perpendicular to the hexagonal planes shows that Li^+ has the potential energy mimina away from such plane.)

We have found that the larger value of Ag^+-ion polarizability yields the lower activation energy, and the larger radius of Na^+-ion leads to the higher activation energy.

The random walk model is used to calculate σ_o for crystals with 16% excess M^+ ions and the results are compared with some reported measured values in Table II.

We have also carried out similar calculations for some crystals with a low concentration of impurity ions. These are listed in Table III.

Table I. Calculated and experimental activation energies of beta-alumina crystals in eV. $E_a(2)$ and $E_a(6)$ are calculated with 2 and 6 M^+ ions, respectively, allowed to adjust their positions.

Material	$E_a(2)$	$E_a(6)$	$E_a(Exp)$
Li-beta	0.29	0.10	0.378
Na-beta	0.27	0.13	0.165
Ag-beta	0.15	0.10	0.176
K-beta	0.32	0.23	0.233
Rb-beta	0.52	0.39	0.311
Cs-beta	1.15	0.81	-----

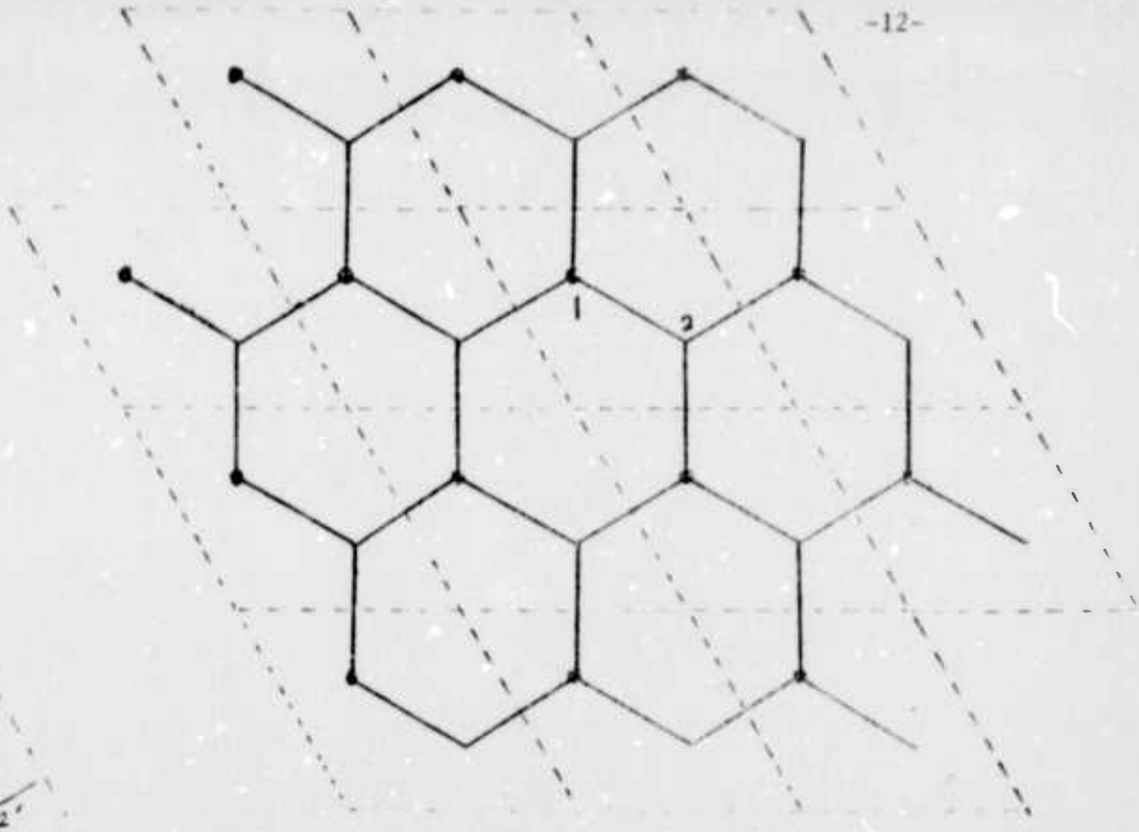
Table II. Calculated and experimental values of σ_o for beta-alumina crystals with n=0.16N. The values are in units of 10^3 $(ohm\text{-}cm)^{-1}°K$.

Material	$\sigma_o(Cal)$	$\sigma_o(Exp)$
Li-beta	6.43	---
Na-beta	2.33	2.5
Ag-beta	1.11	1.6
K-beta	2.13	---
Rb-beta	1.66	---

Table III. Calculated activation energies in eV for K^+ - and Na^+ - beta alumina with impurities. Six metal ions are allowed to adjust their positions.

Material	Complex	Ion	$E_a(6)$
Pure Na-beta	Na^+-Na^+	Na^+	0.13
1 K^+ in Na-beta	Na^+-K^+	K^+	0.22
		Na^+	0.10
Pure K-beta	K^+-K^+	K^+	0.23
1 Na^+ in K-beta	Na^+-K^+	K^+	0.31
		Na^+	0.10

Figure I



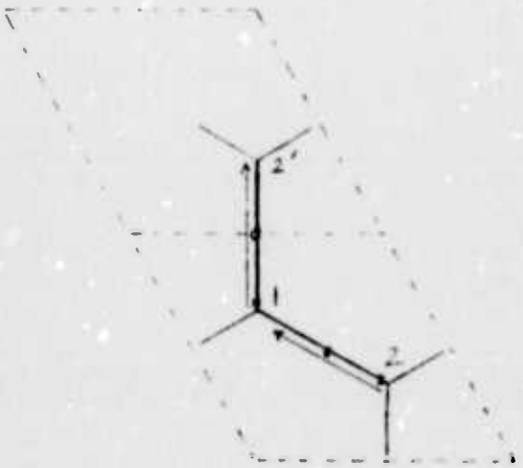
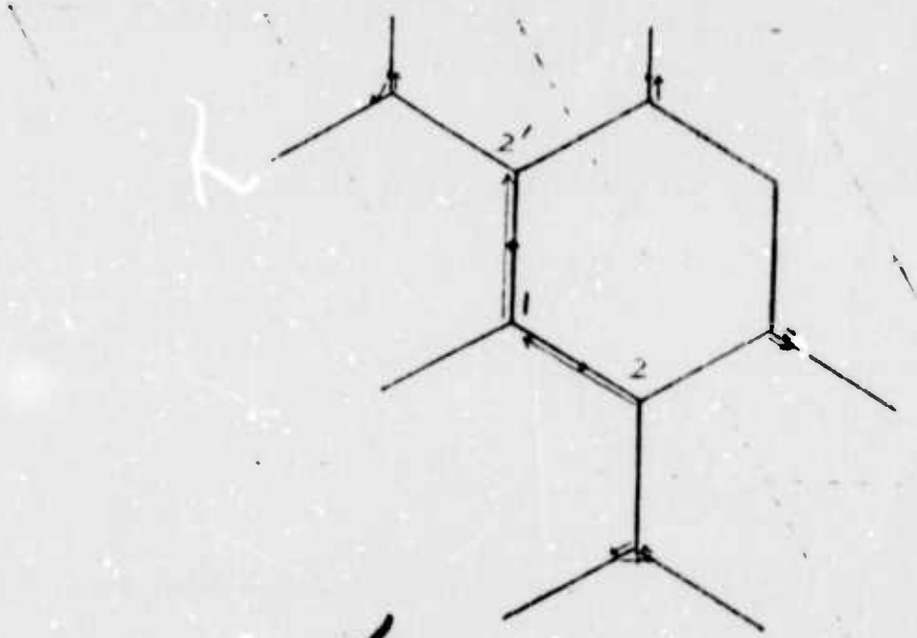


Figure II

Figure III



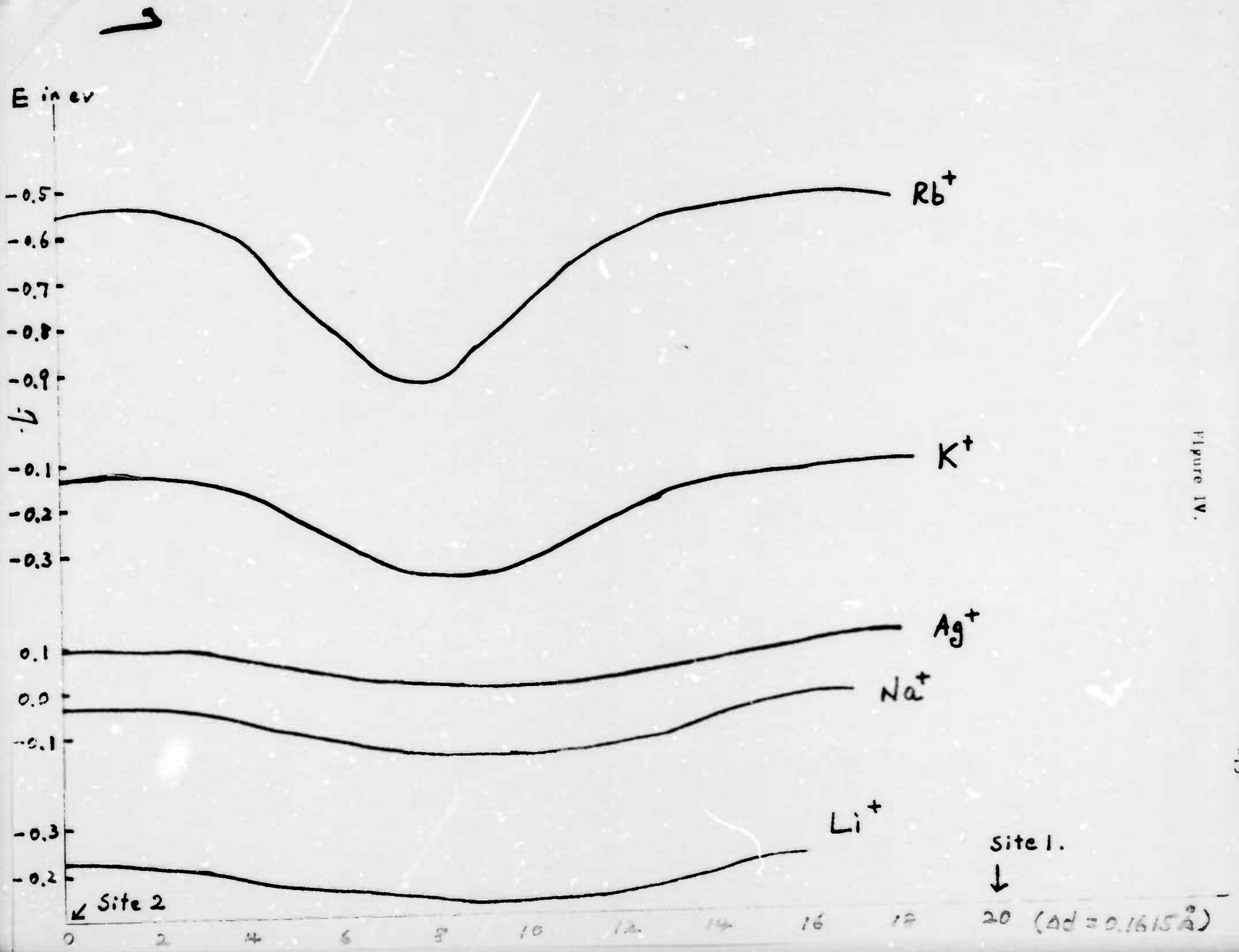

E in ev
-0.5
-0.6
-0.7
-0.8
-0.9
-0.1
-0.2
-0.3
0.1
0.0
-0.1
-0.3
-0.2
Rb+
K+
Ag+
Na+
Li+
Site 2
Site 1.
0
2
4
6
8
10
12
14
16
18
20 (Δd = 0.1615 Å)

Figure IV.

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Publications:

D. E. Dunn, L. J. LaFountain, and R. E. Jackson, "Porosity Dependence and Mechanism of Brittle Fracture in Sandstones," Jour. Geophys. Res., v. 78, n. 14, p. 2403-2417, (1973).

P. J. Roper and D. E. Dunn, "Superposed Deformation and Polymetamorphism, Brevard Zone, South Carolina" Geol. Soc. America, Bull., v. 84, p. 3373-3386, (1973).

L. J. LaFountain and D. E. Dunn, "Anisotropy and the Coefficient of Sliding Friction," Eos, Amer. Geophys. Un., Trans., v. 55, n. 4, p. 428, (1974).

R. E. Jackson and D. E. Dunn, "Experimental Sliding Friction and Cataclasis of Foliated Rocks," Int. J. Rock Mech. Min. Sci., v. 11, (1974 in press).

L. J. LaFountain and D. E. Dunn, "Effect of Anisotropy on the Coefficient of Sliding Friction in Schistose Rocks," Int. J. Rock Mech. Min. Sci., (1974 in press).

Summary of Research Activities:

(1) Dilatancy - Fluid Diffusion Model for Earthquake Prediction.

Recently Nur (Geology, May 1974) has published confirmation of the dilatancy - fluid diffusion model based on data from the Matsushiro, Japan earthquake swarm. His interpretation of the data depends upon assumptions regarding the relation between discharge and pore pressure in a dilating fault zone. Currently we have underway a series of experiments which should confirm or deny Nur's model. These consist of fracture tests in two modes.

In the first we hold pore pressure constant so that water inflow exceeds the rate of pore pressure increase ($q >> d\phi/dt$); while in the second we allow pore pressure to decrease so that $d\phi/dt >> q$. Within a few months we should have firm experimental evidence with which to refine possible earthquake prediction schemes.

(2) Brittle Fracture Mechanisms.

There follows the abstract of the paper cited above by Dunn, LaFountain, and Jackson.

Porosity Dependence and Mechanism of Brittle Fracture in Sandstones. Brittle fracture tests of 105 fine-grained quartz arenites were conducted at 25°C, 1.0 kilobar confining pressure, a constant strain rate of 6.5×10^{-5}/sec., and pore pressure ranging from 0 to 750 bars. Orientation of planar anisotropy (bedding or cross-bedding) with respect to principal stresses has little influence on the fracture strength. The Donath orientation effect depends upon rock type. Strong dependence of fracture strength on porosity is of the form: $y = ax^b$ (where y= stress difference at failure, x= porosity, and $\underline{a} > 0 > \underline{b}$; in our samples values for a ranged between 16 and 25 kilobars, and b between -0.8 and -1.0). Through-going shear fractures result from coalescence of grain boundary cracks, extension fractures within grains, and void space. Rocks with low porosity develop through-going shears only after many grains are extension fractured. The functional relationship between porosity and fracture strength derives from the lower energy required for propagating cracks to utilize void space rather than forming extension fractures.

(3) Frictional Properties of Anisotropic Rocks.

There follows the abstract of the paper cited above by LaFountain and Dunn.

Effect of Anisotropy on the Coefficient of Sliding Friction in Schistose Rocks. Foliated schist samples were sawcut at 45° to the cylinder axis and tested at 500 bars confining pressure, 25°C, and 10^{-4}sec^{-1} shortening rate, to examine the effect of anisotropy on the coefficient of sliding friction (μ_s). Cylinders were cored from sample blocks in a variety of orientations to produce sawcut-to-foliation (STF) angles ranging from 0° to 180° in 15° increments.

The variation of μ_s with foliation orientation is sinusoidal. Maximum values of μ_s occur when the foliation is parallel to principal stress planes (STF = 30° - 45° and 105° - 120°; $\tau = 0$), and minimum values of μ_s correspond to planes of maximum resolved shear stress (STF = 75° and 165°, $\tau = \tau_{max.}$).

Sliding-surface damage and gouge development vary inversely with μ_s. Surface damage results from the interaction of asperities with the sawcut surface, and failure and cataclasis of asperities produces gouge. Precursor events visible on force-time records, and partial loading tests terminated before megascopic sliding, indicate that surface damage and gouge are generated before megascopic sliding on the sawcut. Apparently, high resolved shear stress produces slip along the foliation prior to sliding on the sawcut. Foliation slip generates gouge at the sawcut interface; and the effect of the gouge is to lower μ_s.

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Publications:

"A Nearest-Neighbor Technique Applied to the Reduction of the Number of Standard Solutes Needed to Characterize Gas Chromatographic Liquid Phases," S. R. Lowry, S. Tsuge, J. J. Leary and T. L. Isenhour, accepted by J. Chromat. Sci.

"Progressive Filter Network: A General Classification Algorithm," S. R. Lowry, J. C. Marshall and T. L. Isenhour, submitted to Science.

"Bayesian Decision Theory Applied to the Multicategory Classification of Binary Infrared Spectra," H. B. Woodruff, S. R. Lowry and T. L. Isenhour submitted to Anal. Chem.

Summary of Research Activities

(1) Studies of Gas Chromatographic Liquid Phases

Gas Chromatography has become, perhaps, the most frequently applied separation method in chemical analysis. This technique is capable of separating and identifying components of a great variety of complex samples. The selectivity of liquid phases is typically characterized on the basis of retention behavior, which is desirable because retention behavior directly reflects molecular interactions between liquid phases and test solutes (functional probes) under actual operating conditions. Keller (1) pointed out, "It now seems desirable to characterize the selectivity of mobile and stationary phases in terms of chromatographic behavior, using a minimum number of probe solutes to elucidate the retention forces involved," He also suggested that the selection of these probes might be made by using the extended solubility parameters proposed by Snyder (2).

In a recent work (3) a nearest neighbor technique was used to group liquid employing retention data taken with the first five of McReynolds' solutes (benzene, 1-butanol, 2-pentanone, 1-nitropropane and pyridine) (4). Using these results and other criteria, the authors proposed a set of twelve preferred phases and presented a substitution table listing each of the 226 liquid phases reported by McReynolds with its nearest preferred phase as determined by a five-dimensional distance calculation. A major problem which remains, however, is the systematic characterization of McReynolds, as well as new phases to be reported in the future. Characterizing these phases using the five McReynolds probes would be a task of considerable magnitude. To reduce the amount of work involved the feasibility of using fewer than five of McReynolds probes for the characterization of liquid phases was studied using a nearest neighbor technique.

Two sets of three test probes and several sets of four probes gave results similar to those obtained using all five of the test probes evaluated by McReynolds. The interactive forces important in gas chromatography were related to those solutes present in the best sets of test probes. It is interesting to note that these results obtained using the nearest-neighbor method agree with the work of other researchers who used statistical methods to study retention data.

(1) Leary, J. J. Justice, J. B., Tsuge, S., Lowry, S. R., and Isenhour, T. L., J. Chromatog. Sci. 11, 201 (1973).

(2) Keller, R. A., J. Chromatog. Sci. 11, 49 (1973).

(3) Snyder, L. R., "Modern Practice of Liwuid Chromatography," J. J. Kirkland, ed., Wiley-Interscience, New York, 1971, p. 125.

(4) McReynolds, W. O., J. Chromatog. Sci. 8, 685 (1970).

(2) Progressive Filter Network

With the ever increasing use of computers in all areas of science, applications of pattern recognition have become common in many diverse fields (1,2,3). The goal of any pattern recognition algorithm is to classify objects or patterns on the basis of certain attributes or parameters. Frequently, classification is accomplished by evaluating those parameters with a discriminating function. Unfortunately even after considerable effort and computation time have gone into developing a given discriminant functions, still more lengthly calculations (often requiring a computer) are necessary to classify unknown patterns. Often the scientist who could benefit most, has neither the background nor the equipment to apply these techniques to his own research.

This work describes a pattern recognition algorithm which is conceptually simple and can be applied without resort to a computer. The technique employed is a sequential filter approach.

Each parameter (or dimension) of the data is investigated for an upper and lower threshold. Thresholds are defined as values which will classify only one class of data. The first filter is selected as that which has the two thresholds that classify the most members of the training set. (The thresholds need not classify into the same categories.) These patterns are then removed from the data set and the next best filter is sought.

The network can be applied, once developed, to classifying unknown patterns by following a simple filtering process of companing the magnetudes of individual parameters to the recorded thresholds. Successful applications were made to interpreting mass spectra and electrocardiograms.

(1) Isenhour, T. L. and Jurs, P. C. Anal. Chem., 43 (10), 20A (1971).

(2) Rogers, O. S. and Tanimoto, T. T., Science 132, 1115 (1960).

(3) Jain, V. K., International Journal of Computer and Info. Sci., 2, 231 (1973).

(3) Bayesian Decision Theory Applied to the Multicategory Classification of Binary Infrared Spectra

Pattern recognition techniques employed for the analysis of infrared spectra have been previously reported as acceptable alternatives to search and compare methods (1,2). The advantage of using pattern recognition is the ability to determine common characteristics of spectra from similar compounds. Other compounds displaying similar characteristics in their spectra can then be predicted to belong to the same class of compounds as the original set in which these characteristics were observed. Previous works in this field have reported results using binary classification techniques. This means that the answers were simply yes or no; e.g. yes, the compound was a carboxylic acid or no it was not. Similar questions were asked for esters, aldehydes, and each of the other classes of compounds being tested. For a given spectrum, if after all the questions were answered only one answer was yes, then a specific prediction could be made. Otherwise the prediction would merely be that the compound belong to one of the positive classes.

Another approach is to use multicategory classification techniques. In this case, rather than asking a number of yes/no questions, only one question is asked. To which class does the compound belong? Selection of the proper discriminant function results in a prediction for the correct answer to this question. This paper reports on an investigation of multicategory predictions using binary data. With the knowledge that the spectrum belonged to one of fourteen possible classes, the goal was to select the proper class.

The recognition results obtained using a Bayesian approach were considerably better than the 1% figure expected from random guessing. Bayesian approaches are not used very often, usually due to the difficulty of obtaining $p(A|C)$, known as the a priori probability. However, in a situation such as the one described here, it is quite easy to determine the a priori probabilities from the training set. Given that $p(A|C)$ is obtainable, the Bayesian approach can then be viewed merely as a formalization of common sense (3). If the order 1, 2, 3, 4, 5 most frequently occurs when a compound belongs to class 1, then it is common sense to predict a spectrum giving that same order is of an acid. As was mentioned, the most likely next step for this type of approach would be to use very large training sets incorporating fewer restrictions. Also, the fourteen classes selected for this study would most likely not be the ones selected for a thorough investigation of a large data set. When using a table generated from a large data set, if the percentage of recognition still was near 90% then one would have a quick and accurate means of predicting the type of compound without having to search large numbers of spectra. This study demonstrated the feasibility of employing a Bayesian approach for the classification of infrared spectra, but varying degrees of utility should be found when using discriminant functions generated from other types of data.

(1) Kowalski, B. R., Jurs, P. C., Isenhour, T. L. and Reilley, C. N., Anal. Chem., 41, 1945 (1969).

(2) Liddell III, R. W., Jurs, P. C., Appl. Spectrosc., 27, 371 (1973).

(3) Kelly, P. C., Anal. Chem., 44 (11) (1972).

(4) Failure Analysis of Lubricants

A preliminary investigation of engine oil data was made with the cooperation of the Naval Oil Analysis Program under the Naval Air Systems Command. The body of a report on that initial investigation follows.

The data set investigated consists of information taken from fourteen distinct aircraft engines. Samples of engine oil were analyzed for trace amounts of each of ten elements. The analyses were done by an emission technique. In each of the fourteen cases samples were periodically withdrawn and analyzed until a disabling malfunction occurred. The ultimate goal of this investigation is to determine if any factors involving the given concentrations foretell engine malfunction. To insure practicality the factors need to be simple enough to be visually or graphically seen.

For the following discussion the set of concentrations taken from one oil sample are called a pattern. Also the set of patterns for one engine are designated a subset.

Observations

Consider the nature of the data. The following observations may be made.

1. Some subsets are represented by too few patterns. To distinguish trends, enough patterns must be present to scan the functioning engine before the malfunction. Arbitrarily the four subsets with fewer than four patterns are excluded in data analysis.
2. Engine operation times are not included. For any analysis of concentrations versus time a measure of operation time is needed. Since only the Julian date is given for the patterns, derivative methods will be unreliable.
3. Oil changes appear to be made randomly and oil samples seem to be withdrawn the same way. Concentration profiles have gross jumps where oil is sampled close to the time of oil change.
4. The ultimate cause of engine failure is not given. There is little reason to expect factors indicating one type of failure to be the same as factors for a different cause of failure.
5. There is questionable accuracy in parts of the data. This may be illustrated by observing the set of concentration profiles for silicon. The maximum value for Si is 52 ppm, whereas the other values lie between 0 and 13 ppm.
6. Precision may also be a limiting factor in the emission output data. As a rule of thumb the absolute error may be considered the maximum of 3 ppm and 10% of the concentration.

Investigation of Data

Three methods of data analysis are applied to the data set. Motivation and expectation for each of the three methods are outlined below.

1. If any one element predicts malfunction, then something abrupt should happen to its concentration at the time of failure. Thus a simple look at concentration profiles seems reasonable. The difficulty here is sampling technique (as mentioned in observation three). Little illustrative should result from this look.

2. To overcome the sampling problem, perhaps one of the elements may be set as a standard. This suggests a ratio method---a look at concentration/concentration profiles. It is hoped that as an engine malfunctions, the value of the ratio reaches a maximum/minimum value and that the numeric value of the ratio is significant. A limit to this approach is the large relative error. This will be especially apparent for low concentration species. Ratios between "high" concentration species are preferred.

3. The third procedure assumes that getting to the extreme is less important than how the extreme is approached. Simply this implies a derivative or slope technique. For the given data set two immediate problems exist. Since the derivative operation is especially sensitive to noise, the large relative error eliminates the apparent utility of this method. Further there is no appropriate time function available for the ordinate.

A fourth procedure might be a spectral method. However the quantity of data required for each subset makes this impractical.

Trends

Considering the preceding argument, the concentration ratio procedure (method two above) is preferred. Observation of concentration-concentration ratios are made for the elements of each subset. The denominator is limited to high concentration elements (Cu,Fe,Al,Mg) and all of the 36 remaining ratios are observed. A positive response occurs when for elements X and Y,

$$\left(\frac{[X]}{[Y]}\right)_{\substack{\text{malfunct.}\\ \text{time}}} = \max \left\{\frac{[X]}{[Y]}\right\}_{\text{subset.}}$$

Using this criterion on the ten subsets, [Cu]/[Fe] and [Fe]/[Al] give five positive responses. [Cu]/[Al] and [Cu]/[Mg] give three positive responses.

Considering all the problems inherent in the data these results are encouraging. Unfortunately although the maxima appear, the value at these extrema do not seem to be significant.

At this point the analysis pleads for time factors and a curve smoothing algorithm. This would allow a derivative procedure to be attempted.

It needs to be emphasized that all the afore mentioned results only indicate possible trends. Until an investigation of a larger data set takes place all results are, at best, tentative.

Recommendations

In order to determine whether trends are present or, if present, significant, other factors need to be included in the data. As mentioned previously the engine run times between sample withdrawals and the eventual cause of failure are needed.

Other suggestions concern, either directly or indirectly, the oil change itself. For data analysis it would be ideal if the oil were changed at regular run time intervals and oil sampled immediately before the oil change. It seems that the latter of these is a reasonable suggestion and that the former is an ideal expectation. Some of this problem could be aided by including "standard engines" in the data. The "standard engine" would have its oil changed regularly and sampled immediately before the oil change. Samples could also be taken as a function of time over the life of the engine oil. These would provide normal curves and standardizing curves to compare with curves near malfunction times.

These suggestions intentionally overlook the irreproducibility of the "coffee can" sampling technique. This is an obvious contributor to data scatter and need not be mentioned more.

Conclusions

A first analysis of the data appears to be rather inconclusive. Tentative trends appear, but noise factors impair certainty on such a small and imcomplete data set. Before a final decision may be made more data per pattern and more patterns need to be investigated.

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Publications:

Cheryl B. Damman, Joseph L. Hughey IV, Donald C. Jicha, Thomas J. Meyer, Philip E. Rakita and Thomas Ray Weaver, "Intramolecular Oxidation-Reduction Isomerism in $(P(C_6H_5)_3)_2(CO)ClIr(SnCl_4)$," Inorg. Chem., 12, 2206 (1973).

Gilbert M. Brown, Frederick R. Hopf, John A. Ferguson, Thomas J. Meyer and David G. Whitten, "Metalloporphyrin Redox Chemistry. The Effect of Extraplanar Ligands on the Site of Oxidation in Ruthenium Porphyrins," J. Am. Chem. Soc., 95, 5939 (1973).

F.R. Hopf, J.A. Ferguson, G.M. Brown, D.G. Whitten, and T.J. Meyer, "Photochemistry and Redox Activity of Some Metalloporphyrin Complexes," Annals New York Academy of Sciences, 206, 516 (1973).

J.N. Braddock and T.J. Meyer, "The Kinetics of the Oxidation of $Fe(H_2O)_6^{2+}$ by Polypyridine Complexes of Ruthenium(III). Negative Enthalpies of Activation," J. Am. Chem. Soc., 95, 3158 (1973).

J.R. Pladziewicz, J.A. Broomhead, H. Taube, and T.J. Meyer, "Reduction of Oxygen by Hexammineruthenium(II) and by Tris(ethylendiamine)ruthenium(II)," Inorg. Chem., 12, 639 (1973).

S.A. Adeyemi, E.C. Johnson, F.J. Miller, and T.J. Meyer, "The Preparation of Pyrazine-Bridged, Polymeric Complexes of Ruthenium(II)," Inorg. Chem., 12, 2371 (1973).

W.L. Bowden, W.F. Little, and T.J. Meyer, "Diazonium Complexes of Transition Metals. Diazotization by Coordinated Nitrosyl," J. Am. Chem. Soc., 95, 5084 (1973).

A.R. Burkett, D.G. Whitten, and T.J. Meyer, "Light-Catalyzed Substitution and Disproportionation in $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$," J. Organometal. Chem., 67, 67 (1974).

T.J. Meyer, "Oxidation-Reduction and Related Reactions of Metal-Metal Bonds Prog. Inorg. Chem., in press.

S.A. Adeyemi, G.M. Brown, R.W. Callahan, W.E. Hatfield, and T.J. Meyer, "Oxidation State Properties of Ligand-Bridged Ruthenium Complexes", Proc. XV International Conference on Coordination Chemistry, Moscow, U.S.S.R., June, 1973, p. 251.

J.L. Cramer and T.J. Meyer, "Unusual Activation Parameters in the Oxidation of $Fe(H_2O)_6^{2+}$ by Polypyridine Complexes of Iron(III). Evidence for Multiple Paths for Outer-Sphere Electron Transfer," Inorg. Chem., in press.

G.M. Brown, D.O. Cowan, C. LeVanda, F. Kaufman, P.V. Roling, M.D. Rausch, and T.J. Meyer, "Oxidation State and Electron Transfer Properties of 1,1'-Polyferrocene Compounds," submitted for publication.

R.B. Frankel, W.M. Reiff, J.L. Cramer, and T.J. Meyer, "Magnetic Field Mossbauer Spectroscopy of the Clusters $[(\pi\text{-}C_5H_5)\cdot Fe(CO)]_4$ and $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$," Inorg. Chem., in press.

C.R. Bock, D.G. Whitten, and T.J. Meyer, "Electron Transfer Quenching of the Charge Transfer Excited State of $Ru(bipy)_3^{2+}$. A Flash Photolysis Relaxation Technique for Measuring Very Rapid Electron Transfer Reactions," submitted for publication.

S.A. Adeyemi, G.M. Brown, R.P. Eckberg, W.E. Hatfield, E.C. Johnson, K.T. McGregor, T.R. Weaver, and T.J. Meyer, "Chemically Significant Interactions Between Ruthenium Ions in μ-oxo-bridged Complexes of Ruthenium(III), submitted for publication.

W.L. Bowden, W.F. Little, and T.J. Meyer, "Nitrosoarene Complexes of Ruthenium from the Reaction of Coordinated Nitrosyl with N-Alkylanilines," submitted for publication.

R.W. Callahan, E.C. Johnson, G.M. Brown, T.R. Weaver, and T.J. Meyer, "Polymeric, Mixed-Valence Transition Metal Compounds," A.C.S. Symposium Series, in press.

Summary of Research Activities:

(I) Oxidation of Coordinated Ligands

Detailed studies have been carried out on several reactions involving intramolecular electron transfer from a coordinated ligand to ruthenium(III):

$$Ru(bipy)_2(N_3)_2 \xrightarrow{-e^-} Ru(bipy)_2(N_3)_2^+ : E_{1/2} = 0.17V$$

$$Ru(bipy)_2(N_3)_2^+ + CH_3CN \longrightarrow Ru(bipy)_2(CH_3CN)N_3^+ + 3/2N_2 : k^{25°} = 1x10^4 sec^{-1}$$

$$Ru(bipy)_2(CH_3CN)N_3^+ \xrightarrow{-e^-} Ru(bipy)_2(CH_3CN)N_3^{2+} : E_{1/2} = 0.65V$$

$$Ru(bipy)_2(CH_3CN)N_3^{2+} + CH_3CN \longrightarrow Ru(bipy)_2(CH_3CN)_2^{2+} + 3/2N_2 : k^{25°} = 2\times10^{-2}\ sec^{-1}$$

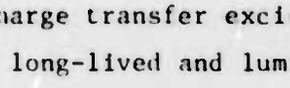
(bipy is 2,2'-bipyridine; the $E_{1/2}$ values are vs. the saturated sodium chloride calomel electrode in acetonitrile)

$$Ru(bipy)_2en^{2+} \xrightarrow{-e^-} Ru(bipy)_2en^{3+} : E_{1/2} = 1.0V$$

$$Ru(bipy)_2en^{3+} \xrightarrow{-3e^-} (bipy)_2Ru\left(\begin{array}{c} H \\ N=C-H \\ \\ N=C-H \\ H \end{array}\right)^{2+} + 4H^+$$

In some cases it has been possible to study the details of the intramolecular electron transfer step since the ruthenium(II) complexes, e.g., $Ru(bipy)_2en^{2+}$ and $Ru(bipy)_2(N_3)_2$, can be oxidized rapidly to ruthenium(III) either chemically (using Ce(IV) or Br_2) or electrochemically. Initial studies have shown that I^-, NCS^-, CN^-, and $C_2O_4^{2-}$ are also oxidized when bound to bis(2,2'-bipyridine)ruthenium(III).

(2) Electron Transfer Quenching of Excited States.

The charge transfer excited state of $Ru(bipy)_3^{2+}$, $Ru(bipy)_3^{2+*}$, is relatively long-lived and luminesces strongly at room temperature in solution. We have studied the quenching of the excited state by a series of quenchers using spectrofluorimetry and flash photolysis. The rates of quenching of the excited state by $Fe(H_2O)_6^{3+}$ and $Ru(NH_3)_6^{3+}$ (in water) and by CH_3-  -CH_3^{2+} and other electron deficient organic oxidants (in acetonitrile) are at or near the diffusion-controlled limit. The quenching of the excited state occurs by electron transfer quenching and the quenching step is followed by a slower dark reaction which takes the system back to equilibrium:

$$Ru(bipy)_3^{2+} + h\nu \longrightarrow Ru(bipy)_3^{2+*}$$

$$Ru(bipy)_3^{2+*} + Ox \xrightarrow{k_Q} Ru(bipy)_3^{3+} + Red$$

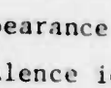
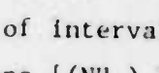
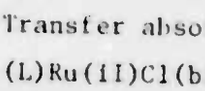
$$Ru(bipy)_3^{3+} + Red \xrightarrow{k} Ru(bipy)_3^{2+} + Ox$$

(Ox and Red are the oxidized and reduced forms of the quencher.)
We have been able to measure k_Q by emission quenching and k by flash photolysis. k values have been obtained for reactions with ΔG changes

of as large as 1.7V. The rate studies on reactions in this ΔG region show that the predictions made by Marcus theory for reactions in the "abnormal" free energy region are incorrect.

(3) Metal-Metal Interactions through Bridging Ligands.

The μ-oxo-bridged complexes of ruthenium(III), $[(bipy)_2XRu\text{-}O\text{-}RuX(bipy)_2]^{2+}$ (X = Cl, NO_2), have been prepared and characterized. From electrochemical studies in acetonitrile the ion $[(bipy)_2XRu\text{-}O\text{-}RuX(bipy)_2]^{2+}$ also exists as mixed-valence +3 (Ru(III)-Ru(IV)) and +1 (Ru(III)-Ru(II)) ions. The chemical, magnetic, and spectral properties of the μ-oxo-bridged dimers can be explained using a molecular orbital scheme based on a strong and chemically significant ruthenium-ruthenium interaction through the bridging oxide ion.

Weak interactions exist between ruthenium ions in the complexes $[(NH_3)_5Ru(L)RuCl(bipy)_2]^{4+/3+}$ where L is a dibasic, N-heterocyclic ligand containing an intact aromatic π-system, e.g.,  ,  , and  . The effects of metal-metal interactions are seen in the electronic spectra of the ions and by the appearance of intervalence Transfer absorption bands for the +4 mixed-valence ions $[(NH_3)_5Ru(III)\text{-}(L)Ru(II)Cl(bipy)_2]^{4+}$. Weak interactions also exist between the iron sites in the mixed-valence, 1,1'-polyferrocene ions $[(C_5H_5)Fe(C_5H_4\text{-}C_5H_4)\text{-}Fe(C_5H_4\text{-}C_5H_4)Fe(C_5H_5)]^{2+/+}$ $[(Fc\text{-}Fc\text{-}Fc)^{2+/+}]$ and $[(C_5H_5)Fe(C_5H_4\text{-}C_5H_4)\text{-}Fe(C_5H_4\text{-}C_5H_4)Fe(C_5H_4\text{-}C_5H_4)Fe(C_5H_5)]^{3+/2+/+}$ $[(Fc\text{-}Fc\text{-}Fc\text{-}Fc)^{3+/2+/+}]$. The mixed-valence polyferrocene ions can exist as a series of oxidation-state isomers which with regard to the site of oxidation. For example, for the ion $(Fc\text{-}Fc\text{-}Fc)^{2+}$ two energetically equivalent isomers exist--$Fc^+\text{-}Fc^+\text{-}Fc$ and $Fc\text{-}Fc^+\text{-}Fc^+$--and one energetically inequivalent isomer exists--$Fc^+\text{-}Fc\text{-}Fc^+$. The existence of oxidation state isomers influences such properties of the mixed-valence ions as their electronic spectra, the position and intensity of Intervalence Transfer bands in the infrared, the presence of statistical effects in measured reduction potentials and rates of intramolecular electron transfer between different iron sites.

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Publications:

R. D. Rieke, S. Uhm and P. M. Hudnall, "Activated Metals. II. Preparation of Highly Reactive Zinc," J. C. S. Chem. Comm., 270 (1973).

R. D. Rieke and S. Babs, "Activated Metals. The Effect of Added Metal Salts on Magnesium Reactivity," J. C. S. Chem. Comm., 879 (1973).

R. D. Rieke and S. Babs, "Activated Metals. IV. Preparation and Reactions of Highly Reactive Magnesium Metal," J. Amer. Chem. Soc., 96, 1174 (1974).

R. D. Rieke and Li-Chung Chao, "Activated Metals. V. The Preparation of Highly Reactive Aluminum Metal and the Direct Synthesis of Phenylaluminum Halides," Synthesis in Inorganic and Metalorganic Chemistry, 4, 0000 (1974).

Li-Chung Chao and R. D. Rieke, "Activated Metals. VI. Preparation and Reactions of Highly Reactive Indium Metal," J. Organometal. Chem., 67, C64 (1974).

Li-Chung Chao and R. D. Rieke, "Activated Metals. VII. Preparation of Trialkyl and Triaryl Indium Compounds Using Highly Reactive Indium Metal," submitted to Synthesis in Inorganic and Metalorganic Chemistry.

Li-Chung Chao and R. D. Rieke, "Activated Metals. VIII. Preparation of Highly Reactive Aluminum Metal and Some of Its Chemistry," in preparation.

R. D. Rieke and S.Uhm, "Activated Metals. IX. Use of Highly Reactive Zinc in the Reformatsky Reaction," in preparation.

Summary of Research Activities:

(1) Chemistry and Technology of Highly Reactive Metal Powders

We recently discovered in our laboratories a new method for preparing metal powders of exceptional reactivity. The basic process consists of the reduction of a metal salt in an ethereal or hydrocarbon solvent with an alkali metal under an inert atmosphere. The boiling point of the solvent must exceed the melting point of the alkali metal used and the metal salt

to be reduced must be partially soluable in the solvent used. Reduction under these conditions yields dark black powders of exceptional reactivity. Magnesium prepared by this method reacts with bromobenzene in five minutes at -78°C, producing a quantitative yield of the corresponding Grignard reagent.

We have extended this area of study to other metals and the studies which have been supported by ARPA include studies on aluminum, zinc, indium, thallium, and titanium.

Reduction of aluminum chloride in xylene yields black aluminum powders of exceptional reactivity. Reaction with iodobenzene at 110°C is complete in 5 minutes; this it to be compared with the literature report that ordinary alumina showings react with neat iodobenzene at 100°C but require 44 hours. A communication on this has been published and a full paper is in preparation.

Use of indium metal in synthesis has had very limited use because of the low reactivity of the metal. We found that reduction of indium salts in xylene with potassium yields indium powders of exceptional reactivity. Reaction of this powder with alkyl and aryl iodides yields the corresponding dialkyl or diaryl indium monoiodide compound in near quantitative yields. A communication on this work was recently published. Also, we have found that reaction of the indium powders with diorganomercury compounds gives high yields of the corresponding trialkyl or triaryl indium compound.

Reduction of zinc salts with potassium in tetrahydrofuran yields black powders which also have unusual reactivity. Rapid reaction with bromobenzene to yield the corresponding phenylzinc bromide indicates the high reactivity as this reaction had not been possible prior to our work. As with magnesium, we found that the reduction of the zinc salts in the presence of alkali salts, in particular LiF, yields zinc powders of ever higher reactivity. The effect of the presence of the alkali salt on the reactivity of the black powders is currently under study. Additional studies with the zinc powders have centered on their reaction with α-halo esters which is known as the Reformatsky Reaction. Use of the active zinc powders allows reactions to be carried out at much lower temperatures and results in much higher yields.

Thallium metal has been used very little in direct synthesis because of its low reactivity. We have found that reduction of thallium (I) salts with potassium in xylene or diglyme yields black powders of exceptional reactivity. The choice of solvent is important as different chemistry is observed depending on the solvent used. The high reactivity of the thallium powders is demonstrated by its reaction with iodobenzene.

Studies with titanium are only of a preliminary nature. However, reduction of $TiCl_4$ in xylene yields black powders which do react with alkyl iodides. This has never been observed before. Additional studies are underway on the chemistry of the Ti powders, and in particular the use of these powders in the fixation of nitrogen.

Extensive studies on the physical properties of the black metal powders are underway to try to determine the high chemical reactivity as well as the apparent high electron transport properties of the black materials. The results are only of a preliminary nature but they suggest that the black materials are a composite material of both the metal and the alkali salt generated in the reduction.