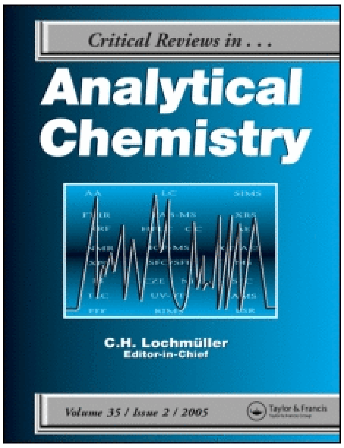

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William F. Pickering; Louis Meites

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HETEROGENEOUS OXIDATION AND REDUCTION PROCESSES; MECHANISMS AND ANALYTICAL APPLICATIONS

Author: William F. Pickering
Trace Analysis Research Centre
Dalhousie University
Halifax, Nova Scotia, Canada

Referee: Louis Meites
Department of Chemistry
Clarkson College of Technology
Potsdam, New York

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I. INTRODUCTION

Many techniques in modern analytical chemistry involve electron transfer in heterogeneous systems. The most important procedures in this classification are those normally grouped under the heading of electroanalytical methods. The basic principles of these particular systems and their expanding value in chemical analysis are constantly under review, and for this reason receive little comment in this article.

The review that follows is restricted to heterogeneous oxidation-reduction processes in which there is no superimposed electrical potential. Apart from sample dissolution, few such reactions are utilized in analysis, and one objective of this review is to consider what is known about the reaction mechanisms in order to explain the current lack of interest in this area.

Relevant mechanistic studies are scattered through the literature, but because the rates of heterogeneous reactions are influenced by many parameters each system can appear to exhibit individual behavior, and the superficial impression is one of general confusion. However, by organizing the published material in a systematic manner it is hoped that readers will discern the interplay of the various factors and be provoked into investigating new analytical applications.

A recent review[1] highlighted the difficulties associated with using thermal techniques in kinetic investigations, and a comprehensive monograph[2] is available on heterogeneous kinetics and the techniques used in such studies.

Apart from any restrictions imposed by the selected technique, similar rate data are apt to be interpreted in different ways by different workers. To understand this, it is appropriate to repeat some oft-forgotten facts about the relationship between kinetics and mechanisms.

Kinetic studies establish the influences of various parameters (concentration, temperature, etc.) on the rate of the slowest step in a reaction sequence, and it is possible for a change in conditions to shift control from one step (or process) to another. The slow step may occur at any stage of the sequence, and its position is indicated primarily by the nature of the mathematical relationship observed between rate and experimental parameters. With many homogeneous systems, the mathematical equations are simple in form and relatively easy to interpret, but this simplicity only occasionally extends into heterogeneous systems.

Derivation of the appropriate mathematical equation *ab initio* can be time-consuming, and hence it is common practice to insert new experimental data into equations already proposed by other workers. Unfortunately, due to experimental errors or the limited number of variables examined, several equations may prove to be equally appropriate.

A reaction mechanism is a series of hypothetical reaction steps, or processes, that lead to a derived rate equation of the same form as that obtained by experiment.

Accordingly, for any given relationship between experimental results, several mechanisms can appear equally probable; a good fit of data to some selected equation does not necessarily confirm the nature of the rate-controlling step or the overall mechanism. For example, an autocatalytic reaction (homogeneous or heterogeneous) leads to a rate curve having a similar sigmoidal shape to that observed in a reaction controlled by the nucleation and growth of a new phase.

II. BASIC PROCESSES IN HETEROGENEOUS REACTIONS

A. Surface Reactions

If one of the reactants is a solid, the initial step in the reaction mechanism is adsorption at the phase interface. Prior to this, the reactive species have to be transported to the interface and in the absence of stirring, or in the presence of porous films, the rate of delivery can control the progress of the whole reaction (cf. Section C).

Should experimental conditions ensure that the rate of mass transport is high, control of the reaction kinetics may lie with the adsorption process.

The retention time for a physically sorbed material is normally very short and there is no significant activation of the molecule. Accordingly, provided that the surface is accessible, the rates of physical adsorption (and desorption) are generally rapid and the heats of adsorption relatively low (few kcal/mol).

With chemisorption considerable changes occur in the distribution of the electrons in the adsorbate molecules, and they become held to the surface by ionic or covalent bonds or dissociate into atoms or radicals bound to the surface by similar bonds. Heats of adsorption are generally high (e.g., >10 kcal/mol) and while some chemisorption processes occur rapidly at all temperatures, others are extremely slow at room temperature and only become significant as the temperature is raised several hundred degrees.

The rate of a heterogeneous reaction can be controlled by the rate of chemisorption, or by that of a later reaction between chemisorbed molecules, radicals, or ions.

Consider an interfacial reaction that involves only species adsorbed on the surface. The simplest reaction one could propose is $A_{(ads)} + B_{(ads)} \rightarrow C$, and if the concentrations of adsorbed species are represented by $(A)_a$ and $(B)_a$, respectively, then the rate of product formation (dc/dt) may be described by an equation of the form

$$dc/dt = k' (A)_a \cdot (B)_a$$

where the proportionality constant k' will vary directly with the surface area exposed (i.e., k' = rate constant x area).

The concentration of reactant at the interface can be related mathematically to the concentration [A] of the species in the fluid phase by means of an appropriate adsorption isotherm. The two most widely quoted are the Freundlich and Langmuir equations, namely

$$x/m = k(p)^{1/n} \qquad \text{[Freundlich]}$$

and

$$\theta = k_1 p/(1 + k_2 p) \qquad \text{[Langmuir]}$$

where x represents the amount adsorbed, m is the mass of solid adsorbent, p is the pressure of gas, n is an integer, and k_1, k_2, and k are constants. θ is the fraction of the number of available surface sites that is occupied. For the sorption of solutes from a liquid phase, the pressure terms are replaced by solute concentrations.

It will be observed that if $(A)_a$ and $(B)_a$ are replaced by appropriate Freundlich isotherms, the rate equation will have concentration terms raised to fractional power terms. On the other hand, if one considers adsorption to follow a Langmuir-type isotherm, it can be seen that at low pressures (i.e., $k_2 p << 1$), the fraction of surface covered (and hence the rate) should vary almost linearly with gas pressure. At high pressure (i.e., $k_2 p >> 1$), θ approaches a constant value and the reaction rate tends to be independent of adsorption control. At intermediate pressures, or where there is competition for sites, the relationship between rate and pressure (or concentration) is nonlinear. With competition for uniform sites, the appropriate forms of the Langmuir equation for two species, e.g., A and B, having partial pressures p_A and p_B, are

$$\theta_A = k_A p_A/1 + k_A p_A + k_B p_B; \theta_B = k_B p_B/1 + k_A p_A + k_B p_B$$

Experimental data derived over a large pressure range can rarely be described in terms of a simple Langmuir isotherm. For such cases the concept of nonuniformity of surfaces can be invoked, but the derived equation contains a large number of adjustable parameters and can be complex in form. In such situations the use of a Freundlich isotherm may be preferable.

It should be emphasized that the products of the reaction can compete for sites, and this requires the addition of a further term to the denominator of the adsorption equation.

There are surface reactions that involve only one adsorbed species [i.e., Rate = $k'(A)_a$], with some possible competition for sites by the product.

In other systems, reaction at the surface is between a sorbed species and a reactant from the homogeneous phase, so that $dc/dt = k[A](B)_a$. Another possibility is reaction between a chemisorbed species and a molecule held briefly in a physically sorbed layer.

Where the product of a reaction is strongly bound to the surface, the surface gradually becomes saturated and control of the kinetics switches from the surface reaction to desorption. In the latter case, the rate can often be described by the Elovich equation, $d(C)_a/dt = k' \exp[-b(C)_a]$, where b is a constant. An equation of similar form is also appropriate for reactions in which the initial adsorption process is the slowest step.

A characteristic of heterogeneous reactions that take place entirely at the phase interface is direct proportionality between the rate and the area of exposed surface, other factors being held constant. In dissolution processes, or in reactions using solid oxidants, particles "shrink" during the course of the reaction and the exposed surface decreases with time. The geometric expression required to relate the exposed area, or interface, to the degree of reaction (a) varies with the shape of the "shrinking particles." For a sphere the effect is describable by $kt = 1 - (1 - a)^{1/3}$ while for a cylinder $kt = 1 - (1 - a)^{1/2}$.

The implications of the preceding discussion can be consolidated by considering the case in which hydrogen gas reacts with a metal oxide to yield metal and water. The overall reaction sequence involves adsorption of hydrogen, abstraction of oxygen from the surface to form water, desorption of this product, and the appearance of a metal phase. If the surface reaction is rate-controlling the rate should be proportional to the exposed surface area and also to the concentration of adsorbed hydrogen. With a static system, using intermediate gas pressures, the amount of adsorbed hydrogen can be defined by an adsorption isotherm, but allowance needs to be made for the decreasing gas pressure resulting from reaction and increasing competition for sites by the product water. The exposed solid surface will also tend to shrink with time. Thus, except at the beginning of the reaction, one could find it difficult to fit the experimental data to any simple mathematical relationship. The same situation would not tend to develop in an experimental set-up in which a gas at a very low pressure flows over a large area of solid. With the flow system, the partial pressures of reactant and product would remain virtually constant, and while only a small fraction of the solid is reduced, there would be marginal change in surface area. The rate of water formation may then be found to vary directly with the gas pressure and weight of solid taken. Please note the mechanism is the same, but there are different experimental parameters leading to rate equations of greatly different complexity (cf. Section E).

The above example is incomplete because the effect of nucleation and particle growth of the new metal phase has been ignored.

B. Nucleation and Growth Processes

A plot of extent of reaction vs. time for the reduction of metal oxides by gases regularly provides an S-shaped logistic curve. This type of curve is typical of reactions in which a product, P, acts as a catalyst for the decomposition of the initial reactant, I. This is, for the reaction

$$I \rightarrow P; -d[I]/dt = k[I][P]$$

In both thermal decompositions and heterogeneous chemical transformations the autocatalytic product tends to be a new solid phase such as the pure metal. Nuclei of this phase are initially produced at localized spots in the sample, and during this time segment (known as the induction period) reaction rates are relatively low and appear to vary linearly with time. At some critical point the catalytic effect becomes pronounced and reaction rates increase rapidly. This acceleratory period reflects the combined effect of two terms, viz., the rate of formation of new nuclei and the rate of growth of existing nuclei. Eventually, the nuclei overlap, the area of interface between the product and reactant phase decreases, and the rate curves display standard exponential decay segments.

Since the rate of growth of nuclei is assumed to be constant, the form of the expression required to describe the acceleratory period is determined by the relationship proposed for the rate of nucleation. In a large number of systems this latter process is regarded as the rate-controlling factor.

Where an active nucleus is formed as the result of the decomposition of a single molecule, the rate of formation of nuclei should follow an exponential law [i.e., $dN/dt = k'N_0 \exp(-kt)$]. On the other hand, where more than one event is necessary to form an active nucleus, nucleation tends to follow a power law [i.e., $dN/dt = k''t^n$]. (N_0 is the total number of potential sites; k, k', and k'' are constants; n is an integer). The multiple events may be successive reactions at the same site, or several decompositions at different sites with the active nucleus being formed through a meeting of these singularities.

In certain cases, nuclei multiply by a chain-branching process, but this soon leads to overlap. A rate equation which allows for this effect has the form $\ln[a/(1 - a)] = kt + c$, where a is the fraction reacted and k and c are constants.

The most popular equation, $\ln(1 - a) = kt^n$ (Avrami-Erofeev), considers nuclei to have a constant rate of three-dimensional growth. In this relationship, n is an empirically determined constant which may vary in magnitude during the course of the reaction.

For systems where the rate of the chemical process is directly related to the surface areas of both the initial solid and the solid product, a rate equation of the following form can be postulated:

$$d\alpha/dt = k(\alpha)^x(1 - \alpha)^y.$$

The values of x and y depend on the value of n in the topokinetic equations quoted above. (For values of n equal to 2, 3, or 4, the exponent x is respectively 0.5, 0.67, or 0.75, and the exponent y has the values 0.77, 0.70, or 0.66).

It has been observed[3] that a few terms are common to most of the mathematical equations that have been developed, and it is suggested that better fits to experimental data can be obtained by using the equation $d\alpha/dt = k(\alpha)^x (1 - \alpha)^y(-\ln[1 - \alpha])^z$.

The magnitudes of the exponents, and any changes that they undergo during the reaction, can be readily ascertained with the aid of a computer. On the other hand, it is usually difficult to postulate the natures of the physical or chemical processes responsible for the changing exponents.

The problem is complicated by the fact that solids are not homogeneous masses. The sites of greatest activity are located near local imperfections, corners, edges, emergent dislocations, etc., and the number of these can be altered by changes in the mode of chemical preparation or by pretreatment procedures such as mechanical processing (grinding, compression into tablets) and heat treatment (annealing, sintering). There is also evidence that reaction rates differ between crystallographic planes. The condition of the starting material can be highly variable, not only in particle size, shape, or surface perfection, but also in total energy.

Also of considerable importance is the porosity of open structured solids and compacts of the materials, for in order to obtain chemical reaction there has to be transport of material into, and from, the advancing phase interface. In heterogeneous oxidations and reductions, diffusion control of the reaction rate is a common phenomena.

C. Mass Transport

The three major processes responsible for mass transport are migration, convection, and diffusion. The driving force in migration is the attraction exerted on charged particles by any potential gradient existing in the system. In the dissolution of impure metals, regions of different potential can occasionally be identified, and then this process may play a significant role. In electroanalytical procedures, which involve applied potentials, the relative extent of migration can be important. The rate of migration depends on the magnitude of the potential gradient, the charge and size of the migrating particles, and, in liquid phases, the degree of solvation.

Mass transport by convection is induced by the flow of a gas or liquid, created by thermal gradients, pressure gradients, or stirring. The process accelerates the delivery of reactants to the phase interface but its effect on the overall reaction rate is difficult to define in quantitative terms. This is due, in part, to the fact that even in stirred suspensions a more or less stagnant layer exists in the vicinity of the phase interface, the thickness of the quiescent layer being a function of the stirring or flow rate.

In quiescent regions diffusion is the most important transport process. Species diffuse from regions of larger to regions of smaller chemical potential, and hence some material is transported by diffusion whenever a concentration gradient exists between two points.

In a stirred solution, the profile of the concentration gradient that extends between the bulk solution and phase interface is probably curved, due to a gradual increase of the degree of agitation as one proceeds away from the interface. This model is a little difficult to handle mathematically, and for the interpretation of kinetic data it is usually sufficient to use the simplification (proposed by Nernst) which assumes that the stagnant layer is kept homogeneous by the stirring action, has a definite thickness (δ), and possesses a linear concentration gradient.

That is, $dC/dx = (C_1 - C_2)/\delta$, where C_1 and C_2 represent the concentrations of the species at the two boundaries of the layer and x is the distance from the phase interface.

The rate dN/dt at which the diffusing species is transported toward a plane surface (of area A) varies with the concentration gradient, so that $dN/dt = A \cdot D \cdot (C_1 - C_2)/\delta$, where the diffusion coefficient, D, varies in magnitude with the size of the species, the viscosity of the medium, the temperature, etc.

It can be difficult to distinguish between diffusion control and first-order reaction kinetics.

Consider the dissolution of a metal in a solution that yields only soluble, nonadsorbed products. The overall rate may be controlled either by the chemical process at the metal surface or by slow transport of reagent to the surface.

For the chemical process, the rate of dissolution (dn/dt) would tend to be proportional to the surface area exposed (A) and to the surface concentration of reactant $(C)_a$, i.e., $dn/dt = k_1 \cdot A \cdot (C)_a$.

With low concentrations of reagent, $(C)_a$ varies almost linearly with the bulk concentration, and the experimental results could show the reaction to be first order in reactant, i.e., $dn/dt = k'' \cdot A \cdot [C]$.

Should the chemical reaction be very fast, convection and diffusion may not succeed in maintaining an appreciable concentration of reagent at the surface. The reaction rate will then be controlled by diffusion across a gradient $([C] - 0)/\delta$. The appropriate kinetic equation in this case is $dn/dt = D \cdot A \cdot [C]/\delta$, and while δ will vary with the degree of stirring, under standard experimental conditions the term D/δ remains fairly constant and the rate equation takes on the form Rate $= k_2 [C]$, where $k_2 = D \cdot A \cdot /\delta$.

Using conditions where the rates of chemical reaction and transport are of similar magnitude, the concentration of reactant at the interface will fall to some equilibrium value C_s, and diffusion transport is promoted by a concentration gradient $(C - C_s)$.

The rates of both processes must balance, i.e., $dn/dt = k_1 \cdot A \cdot C_s = k_2 \cdot A \cdot (C - C_s)$, and by elimination of C_s this yields the expression $dn/dt = k_3 \cdot A \cdot [C]$, where $k_3 = k_1 k_2/(k_1 + k_2)$.

Since the form of the rate equation is similar in each case, it is obvious that criteria not involving this form are needed to distinguish between activated chemical processes and diffusion control.

With diffusion control, changes in the rate of stirring (which alters δ) or in the viscosity of the medium (which alters D) affect the rate, and temperature effects indicate "activation energies" that are smaller (e.g., 3 to 6 kcal/mol) than those observed with most chemical reactions (e.g., 10 to 20 kcal/mol). Distinction is difficult in regions where both processes are important. For example, it has been reported[4] that dissolution of metals in acids less concentrated than 0.1 *M* is diffusion-controlled, that the hydrogen-evolution reaction controls the rate at concentrations above 0.5 *M*, and that control is mixed between these concentrations.

A transition between chemical and diffusion control can also occur when products are not rapidly desorbed and remain on the solid surface as an adherent film. It has been noted previously that with slow desorption the rate is generally expressed correctly in terms of the Elovich equation, and hence it is not surprising to find the data from many surface reactions fitting a logarithmic rate law expression which resembles the integrated form of this equation, viz., $q = 2.303 (\log pK + \log t)/p$, where q is the amount reacted and K and p are constants. If, after initial surface reaction, the rate becomes dependent on a diffusion process, q becomes proportional to $(t)^{0.5}$.

D. Temperature Effects

In kinetic studies it is traditional to evaluate the specific rate constant at various temperatures and to calculate an activation energy from the slope of a plot ln k against 1/T.

For heterogeneous reactions the term "activation energy" has little real meaning, and what is calculated is an "apparent activation energy" or "temperature coefficient of the observed rate constant."

On a surface some regions are more reactive than others, and since solid materials cannot be stirred to ensure thermal homogeneity, "hot" spots can develop at the reaction interface.

Even if this effect is minimal, there remains the problem that an "observed rate constant" is generally the product of a specific rate constant [normally obeying the Arrhenius relationship $k = A \cdot \exp(-E/RT)$] and one or more equilibrium constants.

For example, when reaction in the adsorbed layer is the slowest process, the experimental rate constant contains the constant(s) associated with the relevant adsorption isotherms. Adsorption is an exothermic process and the isotherm constants diminish in magnitude as the temperature increases, in accordance with the exponential of (Q/RT), where Q is the heat released by the chemisorption of 1 mol of adsorbed material. The "activation energies," as determined from Arrhenius plots, can therefore remain constant only over limited temperature ranges. On the other hand, the accuracy is generally sufficient to allow distinction between diffusion and chemically controlled processes.

There is a different temperature effect where the rate-controlling step is the slow adsorption of a reactant or slow desorption of product. The exponential law remains valid (since rate is proportional to $\exp[-b(A)_{ad}]$), but the "apparent activation energy" of the sorption process increases with the quantity adsorbed in accordance with the expression $E = E^\circ + c(A)_{ad}$.

Where heterogeneous reactions are catalyzed by products, temperature has a variable effect. Consider a simple reaction $A + B \rightarrow C + S$ that is catalyzed by the presence of the solid S. The reaction sequence could involve a series of intermediates (I), but for simplicity let us assume a mechanism such as

$$A + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} I; I + B \overset{k_3}{\rightarrow} C + S$$

If reaction 2 is fast while reaction 3 is slow, an equilibrium concentration of I develops at the surface, and it can be shown that the overall activation energy for the system, using low concentrations of reactants, is $(E_1 + E_3 - E_2)$, where E_1, E_2, and E_3 are derived from the variations of k_1, k_2, and k_3 with temperature. When both reaction 2 and reaction 3 are fast, the intermediate is called a van't Hoff intermediate and the overall activation energy for the catalyzed reaction can be shown to equal E_1.

Two other types of heterogeneous reactions warrant brief mention. There are systems in which the surface reaction leads to rapid dissolution of the solid phase, and the rate-controlling step occurs in a subsequent homogeneous reaction. The effect of temperature on these systems tends to deviate from standard Arrhenius behavior only when the rate of dissolution becomes similar to the rate of the slowest solution-phase step.

The final group incorporates those reactions in which the rate is controlled by nucleation of a new phase. For valid application of the Arrhenius equation one has to assume that temperature changes affect nucleation and growth in the same manner and that other physical processes are not involved. The latter assumption is discounted by observations that the experimental rate constant depends on the particle size, packing, and thickness of sample.

E. Experimental Artifacts

As pointed out in preceding sections, changing the experimental conditions can result in a change in the rate-controlling process and possibly a change in the form of the derived rate equation. In many cases the conditions used are dictated by the experimental system selected.

It is not the author's intention to consider techniques in detail, but before proceeding to review the literature on heterogeneous oxidation reactions it is appropriate to consider some generalizations.

With gas-solid systems one has a choice between a flow system and a static system. With a flow system the partial pressure of reactant can be kept virtually constant and the input of fresh gas gives a concentration gradient that favors desorption and removal of gaseous products. Using low pressures of gas, one can accordingly expect to find a direct relationship between pressure and reaction rate. Alternatively, by operating at high pressures and rates of flow of gas, rates should be independent of pressure, and the effects of other parameters may be made more apparent. Static systems are simpler in principle but have the disadvantage that reactant concentration decreases, and product concentration (and possibly inhibition) increases with time.

Since different parameters are effective in each case, the derived rate equations have different mathematical forms. For example, a flow of hydrogen at low pressure over iron(III) oxide leads[5] to a rate equation of the form

$$\text{Rate} = k_1 p_{H_2}/(1 + k_2 \sqrt{p_{H_2}})^2$$

but when flow and pressure conditions make the reaction rate independent of the partial pressure of hydrogen, the appropriate equation[6] is $dx/dt = kx^n$, where x is the fraction reacted and n is a number that varies with temperature and particle size. Some quoted values for n are 0.57 (265 to 315°), 0.13 (300 to 400°, smaller particles), and 0 (400 to 700°).[7] At temperatures above 400°, using hydrogen-nitrogen mixtures, direct dependence of rate on the partial pressure of hydrogen is observed, except in the temperature region 550 to 560°. In this temperature zone it is believed that the effect of increased pressure is balanced by greater adsorption of water by the metastable FeO phase shown by x-ray studies to be present at temperatures between 500 and 570°.

With a static system, the derived rate equation[8] is Rate = $kx^n(a - x)$, where a is the initial hydrogen pressure, x is the amount reacted, and n is a topochemical factor related to the number of reaction nuclei and their rate of propagation. At 265°, very few nuclei are initially formed and n equals unity. At 500 to 600°, many nuclei are formed immediately and n equals 0.

The divergent behavior attributed to the appearance of the FeO phase in the above example has wider implications. To interpret kinetic data it is necessary at times to complement the rate studies with a knowledge of phase diagrams and with physical examination of partially reduced material. In brief, one must confirm the natures of the reaction products obtained at different temperatures. To quote another example, the reduction of Co_3O_4 by hydrogen gives metal only at temperatures below 300°, but gives CoO plus Co at temperatures above 300°. The extra phase manifests its presence by introducing a second maximum into the plots of reaction extent vs. time.[9]

Direct comparison of absolute rates, using different techniques or samples, is extremely difficult because the overall rate is proportional to the available surface area; that is, it is a function of particle size and packing density (d_0). One proposed relationship allows for this factor and has the form[10] $k(C_s - C_e)t = R_0 d_0 [1 - (1 - x)^{1/3}]$, where C_s is the gas concentration at the surface of the pellet, C_e is the equilibrium gas concentration at the metal/metal oxide interface, k is the phase boundary reaction rate constant, and R_0 is the average radius of the particles. With rapid gas flows, the term d_0 has been replaced by $(1 - \epsilon)$, where ϵ is the pore fraction.

It has been pointed out[6] that the reduction of materials such as iron oxide cannot be described solely in terms of a rate determining boundary process; to allow for gaseous diffusion through the reduced layer of metal, it has been recommended[11] that the above equation be modified by adding the term

$$[k \cdot R_0^2 \cdot d_0/k_d]\ [\tfrac{1}{2} - \frac{x}{3} - \frac{(1 - x)^{2/3}}{2}]$$

where k_d is the gas diffusion reaction rate constant.

The densities or porosities of samples can be varied by compaction (i.e., preparation of pellets or briquets) and by sintering. Since these factors influence diffusion rates, sample preparation must be regarded as another important variable parameter. Differences in behavior have been observed among different geometric forms such as pressed plates, pellets, and cylinders of sample. One also has to consider any preheating processes;[12] for example, samples of NiO calcined at 700° are more readily reduced than samples calcined at 800 or 900°.

Another experimental technique for studying heterogeneous reactions is based on the use of a thermal balance. With this equipment the temperature of the sample is continually raised over a period of time, and the interpretative limitations associated with the procedure have been critically examined.[1] Such studies do provide some interesting information. For example, when a single crystal of NiO is heated in hydrogen at the rate of 100°/hr, reaction begins at 300°, gets slower up to about 500° (approximately 45% conversion), then speeds up above 650°. Microscopic studies show that porous layers of nickel powder formed on the (100) plane of the crystal tend to sinter as the temperature rises, thus reducing the number and size of the pores. Escape of water vapor from the inner layers becomes difficult and this process becomes rate-controlling at about 500°. With higher temperatures, the increased water vapor pressure causes enlargement of the pores.[13]

With tablets prepared from 0.5-μm powder, reaction begins at 200° and is 90% complete at 250°. The rate of reduction increases with an increase in compacting pressure. Grinding a single crystal to produce particles 50 μm in size yields a product which reacts faster than the 5-μm material prepared by heating nickel sulfate. The accelerated reduction is attributable to crystal distortions caused by grinding and compaction.

The multiplicity of effects noted in this example serves to emphasize the importance of sample definition and operating conditions.

For reactions involving a solid and a liquid phase, one is generally restricted to a static system, and the major problem is that of ensuring adequate mixing and stirring. With mechanical stirrer bars, vortex formation can delay dispersal and wetting of fine material. Accordingly, early reaction behavior is not readily followed and in some cases very fine material remains as clumps or floats on the surface film for considerable periods of time. High-pressure flow systems would appear to provide on answer to this problem. The rate of stirring can be important (particularly with diffusion control), and hence care is needed to standardize this experimental parameter.

For metal specimens, the stirring problem has been partially overcome by using a rotating sample disc. Advantages of this technique include exposure of a single surface of defined geometry to the reaction mixture and control of rotation speed; disadvantages include eddy currents caused by shaft wobble or surface irregularities, since with a given rotation speed these lead to different diffusion-zone thicknesses and irregular attack on the surface. The many aspects of the rotating disc technique have been considered in a recent review.[14]

In dissolution studies, it has been noted that the overall reaction rate varies in accordance with some power of the disc rotation speed and changes with variations in surface roughness. In some studies a transition from chemical to diffusion control occurs on changing the rotation speed.

Generalizations proposed for gas-solid systems have to be translated to liquid-solid systems with some caution because of the role the solvent can play. Solvent molecules can actively compete for adsorption sites on the solid surface, solute molecules are solvated to differing degrees, and reactions between desorbed products and solute species are encouraged by the liquid medium. The composition of the adsorption layer varies with the nature and variety of species in solution. As a result of these factors competing chemical reactions are the rule rather than the exception. Accordingly, a change in solvent, a change in solute anion, or a change in temperature can be sufficient to yield new products.

The effect that experimental conditions can have on the course of a heterogeneous solution reaction is well-illustrated by the reaction between diarylmethane and manganese dioxide. Refluxing these two reagents at 211° in a solvent mixture (biphenyl and benzene) yields tetraarylethanes:

$$Ar_2CH_2 + O = Mn = O \rightarrow Ar_2\dot{C}H + HO - Mn = O$$
$$Ar\dot{C}H + Ar\dot{C}H \rightarrow Ar_2CH\ CHAr_2$$

Heating the same diarylmethanes with MnO_2 at 125° (without solvent present) gives good yields of the corresponding diaryl ketones.[15] With the lower temperature and no competition from the solvent, the initial radicals tend to interact with the solid instead of desorbing and dimerizing.

As another example, one can quote the reaction between silver "(II)" oxide and ammonia.[16] In alkaline solution, the products are nitrogen, nitrite, and nitrate ions, the proportion of nitrogen increasing with increasing concentration of ammonia. Reduction of the free ammonia concentration through protonation (i.e., formation of NH_4^+) leads to nitrates being the major product, with no observable nitrite, and decreasing amounts of nitrogen. At $pH < 3$, there is a change of mechanism: no nitrogen is detected, nitrate concentrations decrease, and oxygen is liberated.

It is therefore imperative to ascertain the nature of the products before undertaking kinetic studies in heterogeneous systems, and the equilibrium studies should be made using experimental conditions similar to those proposed for the dynamics program. This total information, plus additional physical studies, is necessary if reasonable "tentative" mechanisms are to be proposed.

F. Summary

The apparent discrepancies in the published literature become more explicable when one realizes that with heterogeneous systems a change in experimental conditions can change the identities of the products or the nature of the rate-controlling process.

The multiplicity of the interrelated factors which may influence the course of a reaction or the rate of propagation can be highlighted by listing them, in tabular form, or as components of a flow sheet.

1. Properties of the solid phase – surface area; defect structure (i.e., surface activity); roughness of flat surfaces; particle size; packing density; porosity of surface films.
2. Properties of the fluid phase – gas pressures; viscosity of solvents; number of competing species present; degree of saturation with products.
3. Adsorption phenomena – effect of reactant concentrations; competition for sites by products, solvent, and diverse species; slow adsorption; chemisorption leading to the formation of radicals or compounds; hydrogen abstraction,

oxygen addition, or simple electron-transfer; slow desorption or buildup of surface film.

4. Mass-transport effects – convection and diffusion are influenced by gas flow rates, stirring rates, pore volume, porosity of films, and concentration gradients.

5. Catalytic effects – interfacial reactions leading to nucleation and growth; radical reactions promoted by conducting surfaces.

6. Temperature effects – influences reaction rates, diffusion rates, and magnitude of equilibrium constants; determines nature of stable phases; pretreatment alters surface activity (e.g., annealing of defect structures).

7. Experimental artifacts – flow vs. static systems; nature of fluid phase (single gas or mixtures, pure solvent, or reactive solution); competing chemical reactions.

This list is not exhaustive and omits consideration of groups of heterogeneous systems such as solid-solid transformations and gas-liquid reactions. In the latter case important considerations include gas flow rate, interfacial area (i.e., bubble size), heat of solvation of gaseous species, and chemical reactivity of the gas and solvent phases (see flow sheet on next page).

III. HETEROGENEOUS REDOX REACTIONS IN CHEMICAL ANALYSIS

To be useful in quantitative analysis, a reaction must be stoichiometric and proceed at a reasonable rate. Reactions that do not go rapidly to completion or that are subject to side reactions are soon discarded in most analytical investigations. Examination of possible ways of overcoming the deficiencies is normally justified only if the reaction holds promise of being specific for some type of species or if there is no alternative (e.g., a method of dissolution must be found for a new alloy).

Since few heterogeneous redox reactions satisfy the criteria of speed and simple stoichiometry, the number of recorded applications in chemical analysis is relatively very small. Any relevant mechanistic studies published usually postdate the empirically derived analytical methods and are inspired by motives other than relevance to analytical systems. Accordingly, this critique will be developed in a slightly unbalanced manner. For example, dissolution is a basic preliminary step for a wide range of quantitative techniques, hence a detailed review of dissolution mechanisms is considered to be warranted. At the other extreme, few gas-solid systems have been retained, hence the only mechanisms quoted in this section are those closely related to the known applications.

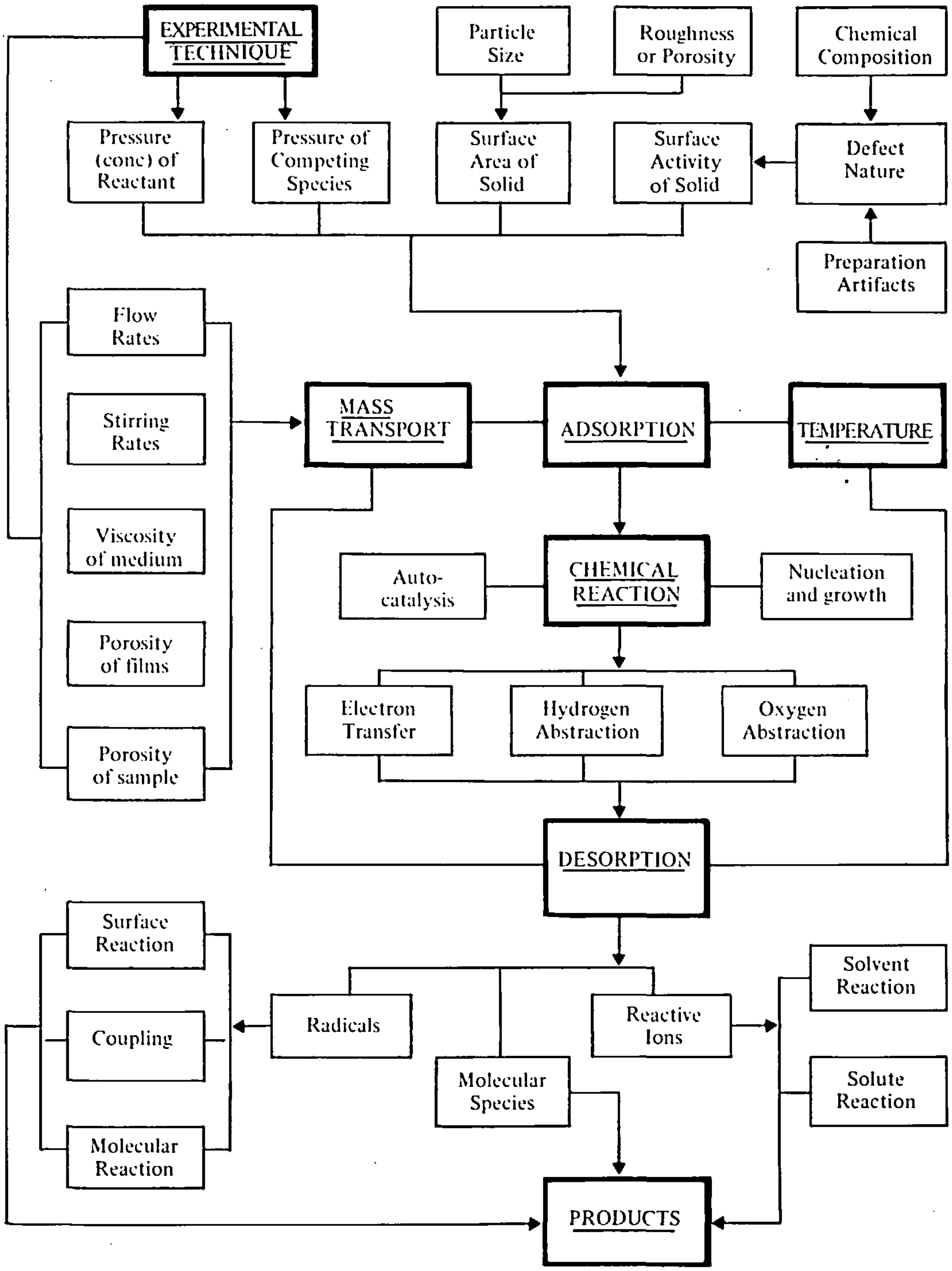
A. Gas-Solid Systems

1. Analytical Procedures

In the Dumas method for determining the nitrogen content of organic compounds, heated copper(II) oxide or nickel oxide is regularly used as the oxidant,[17] the nitrogen liberated being swept into the measuring buret in a stream of carbon dioxide. By operating at 800° in a vacuum, the method can be extended to include the determination of the carbon and hydrogen contents of organic compounds and ammonium salts.[18,19] Earlier workers recommended copper oxide as an oxidant in the analysis of town gas, claiming that the presence of paraffinic gases affected the accuracies of determinations of carbon monoxide and hydrogen only if the samples were rich in hydrocarbons.[20] A modern application utilizes columns of copper(II) oxide (heated to 220 to 300°) to oxidize the carbon monoxide formed in the direct determination of oxygen in organic compounds.[21] The organic sample plus added carbon is pyrolyzed at temperatures greater than 900°. Volatile sulfur compounds in the resultant gases are removed by passage over heated copper or reduced nickel. The hot metal also reduces oxides of nitrogen to nitrogen gas.

The usual method for the determination of the hydrogen content of organic compounds requires the combustion of the sample in a stream of oxygen, but there is an alternative procedure[22] in which samples are heated with magnesium in an atmosphere of argon. The hydrogen so produced is converted to water vapor by passage over copper(II) oxide held at 700°C. The water vapor is then collected and weighed as in the standard procedure.

Satisfactory results for gaseous hydrogen can also be obtained by oxidation of this gas with copper(I) oxide (held at 280 to 290°). Carbon monoxide in the gas mixture is also quantitatively oxidized, but this reaction cannot be used as a means of determination because some of the resulting carbon dioxide is retained by the oxidant mass.[23]


EXPERIMENTAL TECHNIQUE
Particle Size
Roughness or Porosity
Chemical Composition
Pressure (conc) of Reactant
Pressure of Competing Species
Surface Area of Solid
Surface Activity of Solid
Defect Nature
Preparation Artifacts
Flow Rates
Stirring Rates
Viscosity of medium
Porosity of films
Porosity of sample
MASS TRANSPORT
ADSORPTION
TEMPERATURE
Auto-catalysis
CHEMICAL REACTION
Nucleation and growth
Electron Transfer
Hydrogen Abstraction
Oxygen Abstraction
DESORPTION
Surface Reaction
Coupling
Molecular Reaction
Radicals
Molecular Species
Reactive Ions
Solvent Reaction
Solute Reaction
PRODUCTS

Adsorption of carbon dioxide by manganese(IV) dioxide can be so effective that heated columns of activated material have been used to remove the oxides of carbon from gas streams. Silver(I) oxide oxidizes carbon monoxide, in mixtures with air, at room temperature without significant adsorption of the product, but other side reactions render this oxidant unsuitable for quantitative studies.[24]

For analytical purposes the most satisfactory solid oxidant for carbon monoxide appears to be iodine pentoxide.[25-27] Maintaining the solid at 120° allows the iodine formed to be swept along by the gas stream into an iodide solution. The free iodine is determined by titration, and the method is sufficiently sensitive to allow determinations of carbon monoxide, ethylene, and acetylene at concentrations as low as 1 ppm. Iodine pentoxide has been applied to gasoline-engine research[28] and is used in the direct microdetermination of oxygen in organic compounds.[29]

The introduction of new techniques (e.g., gas chromatography and infrared spectroscopy) has provided very convenient methods for the analysis of gas mixtures, and the major role of solid oxidants now seems to be in the field of organic analysis where they serve as reaction accelerators or gas-stream purifiers.

For example, the reaction efficiency for compounds that are hard to convert in oxygen atmospheres to gaseous compounds of carbon, hydrogen, and nitrogen can be increased by mixing the samples with metal oxides (e.g., the oxides of Mn, Fe, Cu, Co, or V). Compounds such as tungstic oxide, silver tungstate, and silver permanganate, when used as tube fillings, serve as adsorption and oxidative aids.[30]

For the determination of the nitrogen content of a solid fuel, preliminary mixing of the sample with manganese(IV) oxide has been proposed.[31]

At elevated temperatures manganese dioxide chemisorbs the oxides of carbon; at lower temperatures these oxides are not retained but the oxides of sulfur and nitrogen are. For this reason, columns of manganese dioxide have proved extremely useful for purifying gas streams prior to adsorption of the water and carbon dioxide formed on combustion of samples.

2. *Studies of Reaction Mechanisms*

Copper(II) oxide is reduced by hydrogen to metallic copper without passing through the intermediate stage of copper(I) oxide. The reaction is autocatalytic, the duration of the induction period and the rate of reduction being influenced by the crystal-defect structure and particle size of the initial oxide.[32,33] The presence of water vapor either extends the length of the induction period or completely inhibits the reaction. The inhibitory effect decreases with temperature, so that above 200° water is reported to have no effect, and it is concluded that the effect at lower temperatures is due to retardation of the formation of nuclei. Carbon dioxide, formed on oxidation of the monoxide, has a similar effect. The reduction of briquets starts at the inner parts of the sample and proceeds along a limited front toward the outer parts, so that even after 90% reduction most of the remaining oxide is in the outer layers.

At low temperatures, below 250°, samples of nickel oxide are also reduced from the inside out by hydrogen gas. The rate of reduction varies with physical parameters such as the degree of compaction of pellets, and there is a distinct induction period. Water vapor inhibits the reaction by decreasing the number of nuclei formed on the solid surface. Below 400° chemical reaction is considered to be the rate-controlling step, while at higher temperatures pore diffusion is an important factor.[34] The effect of experimental conditions is significant, as shown by the fact that reported values for the apparent activation energy range from 5 to 11 kcal/mol (for flow systems) to 26 kcal/mol (for a static system).

For the reduction of nickel oxide by carbon monoxide the activation energy is quoted as 47 kcal/mol at 566 to 682°. The probable reaction sequence consists of formation of nickel nuclei, rapid adsorption of CO at the Ni-NiO interface, migration of the adsorbed CO to the adjacent lattice, and a slow reaction in which oxygen is extracted from the lattice.[35] Carbon is also formed in this reaction, and it has been noted that dissociation of the monoxide requires either an interface (such as Ni-NiO) or prior formation of carbon nuclei. The quantity of carbon deposited is affected by the reduction temperature, reaching a maximum at 450°. The deposition is suppressed by decreasing the feed rate of carbon monoxide or by admixture with hydrogen or nitrogen.[36]

Multiproduct formation becomes more pronounced with polyatomic compounds. When simple paraffins (propane, butane) are heated with copper(II) oxide at temperatures between 320 and 650°, carbon dioxide and water are the main products.[37] The first stage of the reaction follows an exponential law, $dq/dt = a \exp(-\alpha q)$, where a is the initial rate, q is the amount of gas reacted after time t, and α is a constant. The activation energies are of the order of 19 kcal/mol for methane and ethane, and 29 ± 2 kcal/mol for the other paraffins. In the second stage of the reaction it is probable that further oxygen is made available by the migration of Cu^+ from the site of the reaction to an internal Cu_2O/CuO interface. The experimental results fit a rate equation of the form $dx/dt = kb(a - x)/(1 - b)(a - x)$ where k and b are constants and a is the initial concentration; b varies with temperature. The activation energy associated with this stage is 36 kcal/mol for ethane and methane and 27 kcal/mol for other paraffins.

With the higher molecular weight paraffins reaction is incomplete (e.g., only 45% of heptane is decomposed at 400°), and this is attributed to the inhibiting effect of large paraffin molecules adsorbed on the Cu_2O phase. The adsorption of the gaseous products is reversible.

Most of these mechanistic studies used an oxide film on wire; other experiments using powdered oxide led to the formation of metallic copper, the reaction rate varying linearly with time. Activation energies with this substrate are of the order of 40 kcal/mol.

With variations in reaction conditions, the gaseous products, carbon dioxide and water, can react with further paraffin (e.g., methane) to give carbon monoxide and hydrogen. Methane reacts very slowly at temperatures less than 500°; below 600° the time of contact influences the amount of carbon monoxide formed, above 700° the reaction is very rapid, and at temperatures of about 800° the products include acetylene, tar, and carbon (probably arising from radical formation).

While this brief review is probably sufficient to indicate why there are difficulties in obtaining reproducible quantitative results, the indication is strengthened by considering the behavior of manganese dioxide.

The rates of oxidation of hydrogen and carbon monoxide by manganese(IV) oxide are considered to be controlled by diffusion of lattice oxygen;[38] with a continuous flow of gas the rates follow the exponential law quoted above for the copper oxide system. The oxidation of methane by this oxidant begins at a lower temperature than with copper oxide and is complete at 350°, but the reaction is of no value in analysis because of carbon dioxide adsorption. It has been shown by means of CO_2 tagged with O^{18} that this gas exchanges oxygen with MnO_2, possibly through the formation of a CO_3^{2-} group on the oxide surface. In order to allow for the inhibition effect so produced, a rate equation of the following form has been proposed:[9] $dp_1/dt = k(p_1)^m/(p_2)^n$, where p_1 is the partial pressure of CO, p_2 is the partial pressure of CO_2, and k, m, and n are constants.

The reaction between manganese dioxide and hydrogen is first order with respect to the gas, with the rate-determining step being the reaction between adsorbed hydrogen and surface oxygen atoms. The rate constant is a function of the defect order of the sample, the temperature, and the mode of sample preparation.[39]

The oxidation of hydrogen sulfide produces water, sulfur, and manganese sulfide.[40,41] The reaction proceeds inward from the surface and, after the initial surface reaction, the rate is controlled by diffusion of the gas through a porous sulfide ring of growing thickness. In a static system, at room temperature, behavior corresponds to an equation such as $dx/dt = ks$, where $s = (a - x)/[(k\lambda/D) + 1]$, where x is the amount of sulfide formed, a is the initial amount of oxide, s is the surface concentration of H_2S, D is the diffusion coefficient, and λ is the film thickness.

Studies made with other oxides (iron, cobalt, silver, lead, and mercury) further confirm that apart from the reaction with hydrogen, multiple products or complex kinetics are to be expected, and quantitative conversions to specific compounds are likely to be achieved only with highly controlled experimental conditions.

B. Solute-Solid Interactions

1. Solid Oxidants in Chemical Analysis

The use of solids as preoxidants has the attractive feature that excess can be removed by filtration. Unfortunately, side reactions make it difficult to assess the amount of excess required to ensure quantitative conversions, and modern chemists prefer to avoid filtration steps. Column operation could be acceptable in all respects, but with the trend away from "wet analysis," motivation for investigations in this field is comparatively small and many of the published procedures predate 1950.

A solid oxidant which was once used extensively for the oxidation of manganese(II) to manganese(VII) is sodium bismuthate,[42] $NaBiO_3$. In recent years, this oxidation has been critically studied in respect to the determination of manganese in chromium steels[43] and in ferromanganese.[44] Sodium bismuthate has also been used to oxidize cobalt,[45] cerium,[46] and ruthenium.[47,48] In the oxidized state ruthenium can be determined spectrophotometrically, or, if it is present in a sulfuric acid solution of fission products, it can be distilled into sodium hydroxide solution and determined through its radioactivity.

Silver(II) oxide has an advantage over sodium bismuthate in that excess can be destroyed by heating (in acid solutions). In terms of oxidizing power, it can be substituted for the more widely used combination of ammonium persulfate and silver(I) ion as catalyst. Accordingly, it has been used in redox titrations involving determinations of manganese, cerium, chromium, and vanadium.[49,50] Use of this oxidant prior to titration with iron(II) solutions is said to give excellent results for manganese and chromium in aluminum and ferrous alloys.[51] The reagent has also been used in a photometric procedure for phenylcarbazide.[52] In acid media, in the absence of other reductants, silver(II) oxide is reduced by the solvent and liberates stoichiometric amounts of oxygen. Measurement of the volume of gas evolved has been investigated as a means of determining the purity of preparations.[53]

In alkaline media, silver(I) oxide is capable of oxidizing chromium(III) to chromate ion.[54,55]

The reaction between silver(II) oxide and hydrazine yields stoichiometric amounts of nitrogen which can be measured gasometrically.[56] The hydrazine-silver(I) oxide reaction has been used in a similar manner.[57]

Lead(IV) oxide, in solutions buffered with pyrophosphate to pH-values between 2 and 6, has been used[42] to oxidize chromium(III), vanadium(IV), cerium(III), and manganese(II) [to manganese(III)]. The oxidation of chromium(III) with lead(IV) oxide has been studied in both acidic[58] and alkaline media.[59]

Lead(IV) oxide can be substituted for iodine, bromine, or ammonium persulfate to achieve oxidation of nickel ions prior to the determination of this element photometrically, using dimethylglyoxime as reagent.[60]

Methods for the determination of substituted phenothiazines and *p*-acetophenetide based on the color developed on addition of lead(IV) oxide or manganese(IV) oxide have been described,[61,62] but in both cases other oxidants were preferred.

Contrary to this, for the colorimetric determination of manganese, the addition of solid potassium periodate to acid solutions is advocated.[63] If required, any excess of periodate, together with any iodate that is formed, can be precipitated and removed as mercury(II) salts. This reagent is representative of a group of materials which are added as solids, but rapidly dissolve, leading to oxidation in the solution phase.

2. *Solute-Solid Reaction Mechanisms*

The small list of published analytical procedures is due in part to undesirable characteristics (such as low reaction rates, side reactions, etc.) of many solute-solid reactions, and in part to ignorance of the mechanisms involved. Few kinetic or mechanistic studies have been attempted and accordingly, in order to provide an overview of the classes of mechanisms that can be involved, it is necessary to draw on information from other fields, particularly organic synthesis. From the applications listed in a series of reviews,[64-67] it is possible to identify four basic types of mechanism. In each case the first step is sorption of solute species on the surface of the oxide. The selectivity of the process is determined by the physical and chemical properties of the solid, the chemical and stereochemical properties of the adsorbate, and the competition for active sites that is provided by the solvent or by other dissolved species.

Adsorption of solvent or protons can result in rapid dissolution of the solid, with the formation of a solute species that accepts electrons from other solutes. In these *solid-dissolution systems* the solid acts as a controlled source of higher valency ions, the lower rate sometimes minimizing undesired side reactions. For example, the addition of compounds such as chromium(VI) oxide, osmium tetroxide, ruthenium tetroxide, selenium dioxide, potassium periodate, lead(IV) oxide, and sodium bismuthate is recommended for a range of transformations in organic syntheses. Each of these reagents effects its electron transfer through a series of homogeneous steps, many of which are outlined in the monograph by Stewart.[68]

Of the reactions used in analysis, a good example of this group is the silver oxide-hydrazine reaction. Reduction of silver(I) oxide proceeds primarily through silver(I) ions released into solution, and at pH-values above 5.6 dissolution of the solid tends to control the overall rate of reaction.[69] The homogeneous solution reaction proceeds via a series of radical transformations (e.g., $N_2H_4 \rightarrow N_2H_3 \rightarrow N_2H_2 \rightarrow N_2$) and the process is catalyzed by the conducting silver film formed on the walls of the vessel. On a silver film the rate varies with the concentration of N_2H_4 and either Ag^+ ($pH < 5.6$) or moles of oxide (Ag_2O) in alkaline medium. Somewhat similar behavior is observed in hydroxylamine reactions.[70]

With silver(II) oxide there is an initial very fast surface reaction which liberates nitrogen, followed by slower reaction with the solid silver(I) species formed in the first reaction.[71]

After adsorption, solutes can extract oxygen atoms from the solid with a transfer of electrons; that is, *oxidation occurs at the phase interface.*

Oxidations with manganese(IV) oxide usually proceed in this manner. There is evidence from studies using alkaline hydrazine solutions that the reduced layer on the solid surface is only 30 to 60 Å thick;[72] in the reaction with iron(II), pits develop which become deeper as reaction proceeds.[73] Reaction occurs predominantly at special active sites, and the rate varies markedly with the crystalline form of the solid and the anion present. The various polymorphs of MnO_2 are built up from single or multiple octahedral chains joined up along their lengths by the sharing of corners; this leads to three-dimensional frameworks and layer structures. On partial reduction, some of the Mn^{4+} in the framework is replaced by Mn^{2+}, and crystal forms having open structures can act like cation exchangers. The restriction of reaction to the surface zone may therefore be attributable to total or partial blocking of the surface openings to the internal pores or channels.

In aqueous media, the adsorption process can be represented by a Langmuir-type isotherm,[74] with competition for the active sites. For example, iron(II) is considered[75] to form a surface complex $MnO_2 - (Fe^{2+})_2$ which undergoes oxidation to $MnO_2 - (Fe^{3+})_2$. Desorption of the final products (Mn^{2+} and Fe^{3+}) is aided by hydrogen ions, but increasing the acidity decreases the overall rate through its affect on the amount of iron(II) adsorbed. The magnitude of the competitive effect of iron(III) on the oxidation of chromium(III) has been described by the equation[76] $c/A + Kc = (G_O - G)$, where c is the Fe^{3+} concentration, A and K are constants, and $(G_O - G)$ is the difference in the amount oxidized in a given time when iron is present. Other factors affecting the rate of this reaction include pH and concentration of products. A similar equation applies to oxidations with lead(IV) oxide.[77]

Where the products of oxidation contain additional oxygen atoms, these are derived primarily from the surface. This has been demonstrated by oxidizing uranium(IV) ions with MnO_2 or PbO_2 labeled with O^{18}. The resultant product, uranyl ions, contains labeled atoms.[78]

The number of oxygen atoms abstracted by a single entity varies with experimental conditions. For example, shaking water saturated with H_2S with hydrated manganese dioxide produces a mixture of sulfate and thiosulfate ions. If H_2S gas is bubbled through the suspension, a further product, $S_2O_6{}^{2-}$, is observed. On continued addition of gas, the final products become MnS and S, which are the products observed in the absence of water.[79] Passage of sulfur dioxide through an aqueous suspension of the same oxidant yields $MnSO_4$ and MnS_2O_6 as products.[80]

In the above examples, three basic types of surface reaction were illustrated: (1) electron transfer leading to valency change ($Fe^{2+} \rightarrow Fe^{3+}$), (2) oxygen transfer ($S^{2-}$ to $SO_4{}^{2-}$), and (3) hydrogen abstraction ($N_2H_4 \rightarrow N_2H_2 \rightarrow N_2$). These processes are not mutually exclusive and may occur consecutively. For example, oxidation of aqueous ammonia (or ammonium ions) by silver(II) oxide produces a mixture of nitrogen, nitrite ion, and nitrate ion; the amount of each product depends on the concentration of ammonia present.[81] The first reaction is believed to be hydrogen abstraction giving the radical NH ($2AgO + NH_3 \rightarrow Ag_2O + H_2O + NH$). Reaction of this radical with adsorbed NH_3 gives N_2H_4 and thence nitrogen; with low ammonia coverage oxygen abstraction from the surface yields the species HNO, HNO_2, HNO_3.

The formation of radicals at oxide surfaces is so prevalent that *free-radical formation* should be considered as a separate grouping. In most systems, evidence for the existence of radical intermediates is purely circumstantial, being based on the nature of the products or the effects of substituents. Using nickel peroxide,[67] E.S.R.

studies have clearly demonstrated the formation of radicals in a number of organic oxidations. The presence of oxygen atoms in some products indicates that a species like the OH radical may be involved, while in other reactions it is considered that radicals are formed by thermal decomposition and the role of the solid is to provide oxygen atoms.

Radical formation appears to be an integral part of many of the organic transformations listed in review articles,[64-67] but as they invariably seem to lead to multiple products, few of these organic reactions could be considered suitable for quantitative analytical applications and accordingly are not considered in detail here.

Just as there is no clear-cut division between oxygen abstraction and radical-formation systems, there can be equal difficulty in distinguishing between dissolution and surface oxidation. For the latter, one can include a grouping, *simultaneous surface oxidation and dissolution.*

The system of greatest analytical interest which falls in this category is the oxidation of chromium(III) and manganese(II) salts by silver(II) oxide in acid media. The metal ions and hydronium ions compete for the surface sites. Any adsorbed transition metal ions apparently abstract oxygen atoms directly; proton adsorption leads to dissolution and oxidation of hydrated cations by silver(II) ions. The products of the homogeneous solution reaction can be the desired chromate and permanganate, or oxygen released from the solvent. The latter side reaction requires that excess oxidant always be added.[82]

As further mechanistic studies are made, it should be possible to refine the definitions of the various categories, and ultimately to achieve some predictive ability.

C. Selective Reduction Systems

1. Kinetic Limitations

The tendencies of species to accept or donate electrons can be compared by examining tables of standard reduction potentials for the appropriate half-cell reactions; by judicious use of these tables it is possible to select systems which should serve as selective oxidants or reductants. What is not always appreciated is that reduction potentials are thermodynamic quantities and provide no indication of reaction rates. Many reactions that are thermodynamically feasible proceed at such low rates that they have no practical value, while other reactions need to be promoted by catalysts. A further group engages in side reactions with the solvent or with other dissolved species. For predictive purposes, an understanding of reaction mechanisms can therefore be a valuable adjunct to basic tabulations. In the same vein, it is essential that the experimental system be fully defined in order to identify the chemical species involved. A metal covered with a coherent layer of oxide or other sparingly soluble salt will not donate electrons at the same rate as pure metal. Polyvalent ions in solution are likely to exist as hydroxy polymers or complex ions, and if oxygen is transferred in the reduction process the acidity of the solution may influence both the potential and rate of reaction. Foreign ions in solution may be preferentially sorbed onto the surface of a solid and greatly reduce the surface available to the electron-transferring species. With solid reductants, if the foreign species are readily reduced to metal, growth of this deposit creates a surface film of different reducing power.

In terms of reduction potentials, exposure of electron-accepting solutes to different metals should provide many selective procedures, but only in a limited number of cases have the kinetic restrictions been overcome.

2. Dissolution Mechanisms (Nonoxidizing Acid Solutions)

Reduction of a solute by a solid reductant is accompanied by dissolution of the solid (i.e., $M \rightarrow M^{n+} + ne$) and requires that the reduction potential of the oxidizing system (the acceptor) be more positive than the potential of the electron-donating system.

The dissolution of the metal requires ions to be transferred from the metal to the solution interface, i.e., work has to be done to move the ion from its equilibrium position in the metal lattice. Because less energy is involved, local imperfections, edges, corners, emergent dislocations, etc., are probably the sites of highest activity. There is also a work function associated with translating solvated ions in the direction of the surface, and when the phases are in contact there is a point of overlap for the two potential-energy curves. The position of this overlap determines the magnitude of the activation barrier which has to be overcome for transfer between the two phases.

Anion adsorption can accelerate or retard the anodic reaction through its influence on the potential energy curve for the solid phase. Thus, adsorbed anions which tend to form covalent bonds with the surface cause electronic rearrangements which can lower the activation energy. On the other hand, hydroxyl ions, oxygen ions, and oxygen atoms can form such tenacious bonds that a three-dimensional film grows and inhibits the transport of metal ions to the aqueous phase.

An accumulation of hydrogen atoms ($H^+ + e \rightarrow H$) on the surface also constitutes a transport barrier, but this effect can be minimized by adding a "depolarizer" such as hydrogen peroxide, i.e., $H_2O_2 + 2H \rightarrow 2H_2O$.

Depolarizers do not have to react with hydrogen; many serve by providing an alternative cathodic process, as is true of Fe^{3+}, Ce^{4+}, and Cr^{3+}. The preferred reaction process is that which requires the least energy, and a change in solution conditions can be sufficient to vary the nature of this step. For example, reaction of dilute nitric acid with magnesium or zinc yields hydrogen gas; with concentrated acid, oxides of nitrogen are evolved.

With solid reductant systems, the solute of interest has to act either as a depolarizer or as the reactant in the alternative cathodic process. The rate of the process can be controlled by the chemical surface reaction and/or by diffusion, and is a function of reaction conditions as shown in the following summary of some metal-dissolution studies.

Using dilute acids, the rate of dissolution of iron, nickel, and aluminum is predominantly diffusion-controlled since the rates vary with stirring speed and concentration of added depolarizer, and low energies of activation are involved.[83-85] Studies[86] with thin sheets of iron metal indicate that the rate-controlling diffusion process is transport of adsorbed (and absorbed) hydrogen. Depolarizers such as hydrogen peroxide and potassium nitrate overcome this restriction by providing an alternative cathodic process (e.g., reduction of NO_3^- to NH_4^+). With sufficient excess of H^+, the rate can become controlled by the transport of nitrate ions if only low concentrations are present. Conversely, at high stirring speeds sufficient H^+ and NO_3^- can be brought to the surface to provide an oxidation potential which passivates the metal, and higher activation energies (12 to 14 kcal/mol, as compared with 5 to 6 kcal/mol with moderate stirring rates) are observed[87] under these conditions.

Iron, nickel, cobalt, chromium, platinum, and palladium are members of a group of "inert metals" that have a high affinity for electron transitions and act as good reversible electrodes for many redox systems. For this reason, under conditions of natural convection the rate of dissolution of iron in 0.5 *M* sulfuric acid (producing Fe^{2+}) decreases with increasing concentration of iron(III) salts, due to the potential of the metal system (determined by Fe^{3+}/Fe^{2+} redox system) becoming more positive.[88]

In the dissolution of nickel, the process is accelerated by the inclusion of iron(III) chloride, since in this case it serves as a depolarizer.[89]

The order of the rate equation developed for the dissolution of aluminum in hydrochloric acid varies with the experimental conditions.[85] With dilute solutions (<0.5 *M*) the order is 0.5 (or unity if atmospheric oxygen is present). In 1 *M* acid the order is initially 1 but gradually changes to 2. The low energy of activation (6 kcal/mol) suggests diffusion control, but the nature of the controlling diffusion process must vary with conditions. In sulfuric acid media hydrogen peroxide is an efficient depolarizer, but above a concentration of 30% the effect diminishes, probably because of competition between two concurrent processes, the transfer of aluminum ions into solution and the intermediate formation of an oxide barrier.[90]

Dissolved oxygen plays an important role in the dissolution of copper in dilute (0.1 *M*) sulfuric acid solutions. It would appear that two reactions can be involved:

$$2Cu + O_2 + 4H^+ \rightarrow 2Cu^{2+} + 2H_2O$$

and

$$Cu + 2H^+ + H_2SO_4 \rightarrow Cu^{2+} + SO_2 + 2H_2O$$

Between 5 and 35°, chemical reaction is the rate-determining step; above 75° the diffusion of oxygen becomes the rate-determining factor. At intermediate temperatures both processes are significant.[91] On the addition of dichromate ion as depolarizer the rate becomes first order with respect to this ion, and the dissolution process is determined by the rate of transport of this species to the reacting surface.[92]

Iron(III) salts are often used as depolarizers but it has been noted that silver metal does not dissolve in ferric alum solutions as fast as other metals. The reaction $Ag + Fe^{3+} \rightarrow Ag^+ + Fe^{2+}$ does not go to completion (the standard potentials of the two systems are close) but the variations in rate observed with different conditions is best explained in terms of the competitive adsorption of reaction products.[93]

An excess of the dissolving acid can act as an inhibitor. For example, in the dissolution of lead in acetic acid, using hydrogen peroxide as depolarizer, the process is primarily diffusion-controlled, and up to the point where the acid concentration equals the peroxide concentration, the rate increases with increasing acid concentration. In more concentrated solutions of acid (>3 *M*) the rate decreases, apparently due to competitive adsorption by the acid on the lead surface.[94]

The effective potential of a metal-metal ion system can be made more negative by adding a complexing agent to the solution, thus greatly reducing the concentration of hydrated metal ion (an effect predicted by the Nernst equation). The formation of the complex ions also tends to minimize slow desorption or formation of sparingly soluble compounds on the surface.

This increase of the ability of the metal to effect reduction increases the number of species that may undergo cathodic reduction, but in simple acid solutions the rate-controlling step is predominantly the discharge of hydrogen gas (the rate of which is normally expressed in terms of hydrogen overpotentials). Thus, it has been observed that the rate of dissolution of zinc in solutions containing HCl and NH_4Cl (pH 2) is increased by the presence of ions such as As^{3+}, Sb^{3+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Fe^{2+}, Cd^{2+}, In^{3+}, Pb^{2+}, Tl^+, and Hg^+. The magnitude of the increase decreases in the order given and follows the pattern of increasing overvoltage on the metal deposit formed in the initial reaction.[95]

To obtain dissolution it is not essential to have protons present. For example, zinc dissolves rapidly in an ammoniacal solution containing ammonium chloride and sodium nitrate, the primary cathodic reaction being the reduction of nitrate to nitrite.[96]

The reduction of nitrate ions is the predominant cathodic process in dissolutions with nitric acid, and, since this inhibits reduction of other solute species, discussion of mechanisms involving this acid is not relevant to selective reduction studies and is considered in the next section.

For selective reduction it is also desirable to minimize hydrogen evolution since this constitutes a competition for specific solute reduction. As noted above, one way to retard gas formation is to have present a surface such as mercury or lead, on which the overvoltage for hydrogen evolution is high. By coating a metal surface with mercury, or by forming a liquid amalgam, it is possible to combine the benefits of having a clean conducting surface and high hydrogen overvoltage with the reducing power of metals such as lead, cadmium, or zinc.

Liquid amalgams containing 3 to 4% of metal reductant can be used effectively in acid media with minimum liberation of hydrogen. Efficient mixing of the phases and subsequent separation are problems that are overcome in part by use of a column procedure. In the columns, the oxidant species flows slowly through a packing of granulated metal precoated with a mercury film.

After reduction, the lower valency species can be determined through titration with a standard solution of an oxidizing agent.

3. Analytical Applications of Solid Reductants

Maximum interest in analytical applications arose in the preinstrumental era when oxidation-reduction titrations were widely used in routine analysis, and a comprehensive review which appeared in 1952 embraces most of the relevant publications.[97]

The changes in valency state which have been achieved using various metal reductors are summarized in Table 1. To provide some logical framework, approximate reduction potentials are quoted for the various systems. The values reported do not allow for effects which may be predicted from the Nernst equation, for example, the more negative potentials attributable to the formation of sparingly soluble compounds or stable complexes, or for the effect of pH on half-cell reactions such as

$$BiO^+ + 2H^+ + 2e \rightarrow Bi + H_2O;\ E^{\circ\prime} = 0.32\ V$$

In this particular system, the effective reduction potential gradually becomes more negative as the pH is raised above 2. With mercury and lead,

TABLE 1

Reduction of Ions by Metals and Amalgams

		Nature of oxidant species											
Reductant	Approx. E′ (V)	Mn (VII) 1.5	Cr (VI) 1.3	V (V) 1.0	Fe (III) 0.8	Mo (VI) 0.5	U (VI) 0.3	Cu (II) 0.2	Sb (V) 0.2	Sn (IV) 0.1	Ti (IV) 0.1	W (VI) 0.0	Notes a
Hg	0.9				(II)								
Ag	0.8			IV	(II)								
Cu	0.3				II	–							
$Hg/Hg_2C\ell_2$	0.3		III	IV	II	V	IV	I	III		(III)	V	b
Bi-Hg	0.3	II	III	IV	II	V, III	IV	I		II	(III)	V	
$Ag/AgC\ell$	0.2	II	III	IV	II	V, III	IV	I	III		IV	V	
Sb	0.2			IV	II	III	IV			II	III	$\underline{\text{V}}$	
Sn–Hg	-0.1	II	III	II	II	III	IV	I	III	II	III	III	
Pb–Hg	-0.1	II	III	II	II	III	IV	I			III	III	b
Pb	-0.1	II	III	II	II	III	IV			II	III	III	b
Ni	-0.2			–	II					$\underline{\text{II}}$			
Cd–Hg	-0.4	II	III	II	II	III	IV	0		0	III	III	
$Ag/Ag(CN)_2^-$	-0.4		–										
Hg/HgCN	-0.4										—		
Zn–Hg	-0.8	II	II	II	II	III	IV, III	0	III, 0	0	III	III	c
$Cu/Cu(CN)_4^=$	-1.1												
$A\ell$	-1.7				II								

a. Approximate potential for first valency change; horizontal lines indicate regions for subsequent reduction.

b. Strong hydrochloric acid solutions, e.g., >6*N*.

c. Metals deposited include As, Se, Te, Au, Pt, Pd, Rh, Ir, AsH_3 and SbH_3 also formed.

( ) Reaction incomplete except under special conditions.

precipitation of oxide does not become significant until the pH is >6 above which value the effective potential of the system grows more negative.

The magnitude of the precipitation effect is well illustrated by the silver system. In nitrate media $Ag^+ + e \rightleftharpoons Ag$; $E^\circ = +0.8$ V; in the presence of HCl the couple becomes $AgCl + e \rightleftharpoons Ag + Cl^-$, $E^{\circ\prime} = +0.22$ V. Substitution of HBr lowers the potential by a further 0.13 V.

The formation of stable anionic complexes by the metal ions has a similar effect. Thus, the effective reduction potential for copper decreases from +0.3 (Cu^{2+}/Cu system) to -1.09 in alkaline cyanide solution. Proton involvement or complex formation can also alter the potential of the initial oxidant species.

The analytical chemist may therefore increase selectivity by changing the experimental conditions. Conversely, a change in conditions may reduce the effective potential to a value that introduces increased interference effects. A silver reductor, for example, reduces Mo(VI) to Mo(V) using elevated temperatures and hydrochloric acid concentrations of 2 to 3 *M*; with 4 to 10 *M* acid the final product is Mo(III).

If the aqueous solutions contain air, a side product of the reduction process can be hydrogen peroxide, which causes errors in any subsequent titration of the reduced material with oxidants such as potassium permanganate. Many of the reduced species are also subject to rapid reoxidation by air, and for these, reduction in an inert atmosphere is necessary. Alternatively, using the column technique, the solution may be collected into a ferric alum solution and the resulting Fe(II) determined.

Quantitative reductions are not restricted to cations. Wood's metal (alloy of Bi, Pb, Sn, and Cd) and cadmium amalgam (15%) have been used to reduce anions such as chlorate, bromate, and iodate to the corresponding halides, which are subsequently titrated with standard solutions of silver nitrate. The reduction of perchlorate requires the presence of some trivalent titanium ion.

Several procedures have been proposed for the determination of the phosphate content of samples. The methods are based on the initial precipitation of ammonium phosphomolybdate or uranyl ammonium phosphate. The washed precipitates are subsequently reduced in acid medium, using bismuth, lead, cadmium, or zinc amalgams to produce an equivalent amount of lower valency molybdenum or uranium. These ions are then reoxidized with a standard titrant solution.

Organic compounds such as *m*-nitrotoluene, *o*-nitrobenzoic acid, and nitrobenzene have been converted to the corresponding amines by passage through a cadmium reductor and determined through titration of the amines with standard KBr-$KBrO_3$ solution. Indigo, in dilute sulfuric acid medium, is reduced to indigo white, and may be quantitatively determined by titration with an iron(III) solution.

Titanium(III) solutions, prepared by reduction with metal amalgams, have been used to titrate iodate, bromate, chlorate, chromate, methylene blue, and nitro compounds. Chromium(II) solutions can be substituted for the titanium(III). The reductant ions (known volume) are added in excess to solutions containing, for example, picric acid, *p*-nitroaniline, *p*-nitrophenol, or dissolved oxygen, and the amount in excess is determined by titration with standard ferric alum using thiocyanate ion as indicator.

After the solid phase has been separated from reduced solutions the analyst has a choice of titrant, and if several reduced species are present, selectivity may be achieved by using an oxidant of intermediate potential. For example, if a solution contains iron(II) and titanium(III) [or uranium(IV)], the titanium (or uranium) can be determined by titration with iron(III) solutions. The total amount of reduced material can be estimated by titration of another sample with standard iodine (or potassium permanganate) solutions. In the differential titration method developed for the determination of vanadium and molybdenum in iron and steels the titrants recommended are permanganate and vanadate solutions. In this case advantage is also taken of the different reduction potentials of cadmium and bismuth amalgams. Since vanadium is reduced to V(II) by one and to V(IV) by the other, there is a resultant difference in titer which can be used to determine this element. Reduction of separate aliquots with zinc and bismuth amalgams has facilitated determinations in mixtures containing uranium and titanium or iron and vanadium (e.g., in ferrovanadium).

Most applications of solid reductants have been concerned, however, with solutions containing one reducible species.

Finely divided copper reduces iron(III) to iron(II), but the most interesting aspect of this element is the activating effect it exerts when present in metal reductor systems. For example, in the presence of copper, bismuth amalgam reduces iron and titanium; lead and iron reductors completely reduce molybdenum, vanadium, and uranium in addition.[98] A subsequent study showed that gold is a better activator than either copper, silver, or platinum.

The bismuth-amalgam reductor has been applied to the determination of tin, copper, tungsten, vanadium,[97] iron,[99] and molybdenum.[100] Reduction of these elements, together with titanium and uranium, is obtained on boiling acidic solutions with antimony in an atmosphere of carbon dioxide.[101] Lead and nickel achieve the same transitions, but at differing rates in some cases. For example, iron and tin have been determined in the same solution by first reducing the iron at room temperature with nickel and subsequently boiling the titrated solution to effect reduction of the tin.[102]

Reduction by lead has been applied to the determinations of tin in titanium alloys[103] and of uranium in uranium-zinc alloys[104] and other materials;[105] lead has been used as a general reductant.[106]

The silver reductor, introduced by Walden et al.,[107] has proved useful for the determination of iron in the presence of titanium (which is not reduced), and in the absence of interfering substances may be used to determine vanadium, tungsten,[108] molybdenum, uranium, and copper.[97] Antimony has been determined in the presence of arsenic and tin,[109] and the use of a microreductor for the determination of trace amounts of iron[110] has been critically evaluated. Using hydrobromic acid media, quantitative reductions of iron, copper, uranium, and vanadium are achieved;[111] the reduction of molybdenum requires heating.

Tin amalgam[112] and metallic tin have proved satisfactory as prereduction agents in determinations of iron, molybdenum, and uranium and for the analysis of copper alloys. The amount of oxidant reduced can be ascertained by titration of the tin(II) formed in the process; this allows results to be obtained for elements (such as platinum and gold) that are reduced to the metallic state.

Cadmium amalgam[114] has been reinvestigated by a number of workers,[115,116] and it has been noted that ammonium ions, phosphates, and fluorides interfere in the reduction process. Applications include determinations of iron, titanium, uranium, tungsten, molybdenum, and vanadium.[97]

The zinc reductor, when used in the presence of 0.25 to 1 M sulfuric acid, has been widely employed as a preliminary prereductant in determinations of iron, titanium, molybdenum, chromium, vanadium, and uranium. During reductions of uranyl salts some uranium(III) is formed; while this can be readily oxidized to U(IV) with a stream of air, several elements [Mo, Ti, Nb, Cr] induce the oxidation to proceed to the hexavalent state and thus should be absent in uranium determinations. Tungsten(VI) and niobium(V) are reduced to indefinite valency states and consume titrant (often $KMnO_4$) if present. Ions of more noble elements [Cu(II), As(III), Sb(III), Sn(IV)] are reduced to the metallic state. Nitrate ions are reduced to NO, and arsenic and antimony form some volatile hydrides, probably AsH_3 and SbH_3.

In an atmosphere of carbon dioxide, vitamin B_1 is reduced and liberates hydrogen sulfide which can be collected and titrated.[117]

In alkaline solution, antimony(V) is reduced to the trivalent state and can be quantitatively determined by titration of this species.[118]

According to its reduction potential, finely divided aluminum should be a highly active species, but its protective coating of oxide tends to slow down the reaction rate. It is capable of achieving the same reductions as zinc amalgam, hence any applications of it are subject to the same interference effects. Published procedures using this metal include the determinations of iron,[119] molybdenum,[120] and tin.[121]

The increase of reducing power that results from complex formation can be useful for quantitative purposes. For example, in an alkaline cyanide solution activated copper can displace cadmium but not zinc,[122] and mercury reduces ferricyanide ions to ferrocyanide ions.[123] In a hydrochloric acid solution, the reduction of iron(III) by mercury is promoted by the addition of thiocyanate ion.

Where amalgams are used as controlled-potential reductors, the extent of reaction can be evaluated by titration of the metal ion released with EDTA solutions. This approach can be applied to both inorganic and organic systems.[124] For example, p-nitrophenol may be determined by shaking the sample in a deoxygenated acetate buffer with zinc amalgam for 5 min (giving p-aminophenol and zinc ions which are readily titrated).

The gaps left in Table 1 clearly demonstrate that many systems remain to be investigated, and through variation of the nature of either the complexing ligand that is present or the titrant that is chosen, many new procedures could be developed. However, the probability that any such procedure will possess properties that represent a marked improvement on the existing approaches seems to be minimal, unless some radical change in approach is made. Some questions that deserve answers are, how many of the reduction processes used in organic synthesis can be adapted for function-group analysis, what is the effect of a solvent change, etc.?

The technique of titrating the reductant ions instead of the reduced species enhances the scope manyfold, and development of more microprocedures would detract from the criticism that selective reduction is primarily of value for macrodeterminations of a limited number of elements.

4. Redox Resins

In 1949, a polymerized resin that could be oxidized or reduced by the iodine-iodide system was prepared.[125] Subsequent preparations (based on condensations of hydroquinone, pyrogallol, resorcinol, or pyrocatechol with phenol and formaldehyde) proved capable of being oxidized by iron(III) chloride, dichromate ion, or cerium(IV) sulfate, and subsequently reduced by treatment with titanium(III) chloride or hydrazine.[126]

Other materials have been made which incorporate two valency states of a metal ion (e.g., the iron or copper systems) or an organic couple such as methylene blue/leucomethylene blue.

While the principle of these resins is attractive, to date few applications of them have been recorded. In general, their reactions are extremely slow and the resins are not very stable. For quantitative studies, further disadvantages are that the reduction potentials are not only quite positive (which restricts their utility) but also vary with the degree of reaction. In 0.5 M H_2SO_4, the hydroquinone-phenol-formaldehyde resin has a reduction potential $E^{o\prime}$ of 0.65 V which tends to vary in accordance with $E = E^{o\prime} + (RT/nF) \ln[x/(a - x)]$, where a is the total capacity of the resin and x is the amount present in the oxidized form.

D. Dissolution Procedures Involving Chemical Oxidation and Reduction

The dissolution of metals, alloys, and oxides in acid represents the most widespread application of heterogeneous oxidation and reduction in classical chemical analysis.

Metal systems with negative reduction potentials (against S.H.E.) are sometimes classified as "active metals" since they can reduce hydronium ions and liberate hydrogen. For the dissolution of metals having positive reduction potentials (such as Cu, Ag, Au, and Hg) it is necessary to introduce other oxidizing species into the acid media.

The principal "oxidizing acids" are nitric, hot concentrated sulfuric, and hot concentrated perchloric acid. With nitric acid the potential of the nitrate ion-nitric oxide couple may be employed as a rough index, or if mixed with hydrochloric acid some free chlorine is produced and the governing couple is the chlorine-chloride system.

With these acids, oxygen transfer can result in the formation of sparingly soluble oxides (e.g., those of Sb, Sn, and W) or surface films which retard further reaction. In some cases the effect of films can be minimized by adding a ligand such as fluoride ion which forms soluble complexes.

Oxides tend to resist solution in oxidizing acids and dissolve most readily in acids such as hydrochloric. The rate at which an oxide dissolves is often a function of its state of subdivision and the time and temperature of any previous ignition. To achieve a high rate of dissolution a very high temperature such as 1,000°C may be required. This can be achieved in a sealed tube, but more commonly fusion with a flux is used.

1. Dissolution Mechanisms (Oxidation and Complex Formation)

With unstirred solutions, the rate of attack of a 1 *M* nitric acid solution on a metal varies with the reduction potential of the metal, and a plot of the logarithm of the rate vs. potential gives a smooth continuous curve for the series Mg, Al, Zn, Cr, Fe, Cd, Tl, Ni, Sn, Pb, Cu, Ge, Ag, Hg, and Pd. Metals that have reduction potentials more positive than +0.9 V do not dissolve. Metals with a potential more negative than thallium are generally subject to diffusion-control, whereas metals having a more positive potential are governed by chemical kinetics.[127]

The transition point between the two rate-controlling processes is not sharply defined, but there are some obvious differences in the dependence of rate on acid concentration. In the dissolution of aluminum and iron (diffusion-control) the rate varies directly with the concentration of dissociated acid. With nickel, the rate of solution is proportional to the square root of the acid concentration; the rate with copper and molybdenum tends to vary with the concentration of undissociated HNO_3 molecules.[128] In the latter case the first step is the production of HNO_2 which acts as an autocatalyst.[129]

The nature of the products obtained in the reaction of lead with nitric acid varies with the acid concentration, being mainly N_2O (~70%) and N_2 (10 to 20%) with smaller amounts of NO, H_2, and ammonium ion. Protons and adsorbed nitrate ions are considered to participate in the reduction process through a reaction such as $2HNO_3 \rightarrow NO_3^- + NO_2^+ + H_2O$, with the NO_2^+ being rapidly reduced thereafter. The slowest stages are the adsorption of nitrate ions and the electrochemical reaction (activation energy about 13 kcal/mol). A change to diffusion control occurs on increasing the acid concentration to 40 to 60%. The rate of dissolution then varies with the square root of the stirring speed, the activation energy drops to about 8 kcal/mol, and the slow process is probably removal of lead nitrate from the surface.[130]

Germanium metal becomes passive (probably due to a layer of GeO_2) when placed in nitric acid more concentrated than 7 *M*. With dilute acids, the rate of dissolution increases with concentration and the process is controlled by the reduction of nitric acid,[131] possibly by a reaction such as $HNO_3 + HNO_2 \rightarrow 2NO_2 + H_2O$, with the charge-transfer process being $NO_2 + e \rightarrow NO_2^-$.

Dissolution of the more noble metals such as Cu, Ag, and Au can also be achieved using only solutions of complexing agents, but in these cases dissolved oxygen plays an important role. For example, in the dissolution of copper in aqueous ammonia, the cathodic reaction is reduction of oxygen at the surface: $\frac{1}{2}O_2 + H_2O + e \rightleftharpoons 2OH^-$. Unless high partial pressures of oxygen are used, the rate of dissolution is determined by the rate of diffusion of oxygen. As might be expected, the process is inhibited by sulfide ions since these react to give a film of CuS on the surface. There is no clear evidence whether it is a copper (I) or copper(II) species that is formed on rapid chemisorption of the oxygen, but it is observed that the reaction is first order with respect to complexing agent, and the rate-determining step is believed to be chemical attack on the oxygen-covered surface.[132-135]

In the dissolution of silver and gold in cyanide solutions the rate is also considered to be determined by transport processes, either the diffusion of oxygen (in the presence of excess cyanide) or the migration of cyanide ion (using high oxygen pressures).[136]

A single electrolyte can serve as both depolarizer and ligand source. For example, dissolution of palladium in iron(III) chloride yields $Fe[PdCl_4]$, and the reaction is first order with respect to both iron(III) and chloride ions. In the absence of excess chloride ion (added as, for example, NaCl or HCl) the rate is limited by the initial ionization step; in the presence of excess chloride the limiting step appears to be the formation of the complex ion.[137]

Diverse ions in solution often inhibit the dissolution process by competing for active sites on the metal surface, but few attempts have been made to study this effect quantitatively.

2. *Sample-decomposition Procedures*

Information on procedures for dissolving various classes of inorganic materials is provided in a number of books.[138-140] Many of the methods are essentially acid-base reactions and fall outside the scope of this review. With metals and alloys, however, electron transfer is the dominant process. The nature of the acid required is determined in part by the reduction potentials of the constituent elements, in part by the chemical behavior of the resultant metal ions, and in part by the nature of the subsequent analytical steps. Accordingly, Table 2 merely attempts to summarize some general applications and provide a broad subdivision between systems in which the most significant process is hydrogen liberation, reduction of oxidant species, or removal of reaction debris.

The destruction of organic compounds as a preliminary to elemental analysis is also a heterogeneous redox reaction. Dry methods and wet methods are available, the choice being dictated by the type of material being used and operator preference. Table 3 summarizes some of the approaches available, greater details being available in reference books.[138,141,142]

For the determination of C, H, and N the standard procedure, based on oxidation by a stream of oxygen in a heated tube, is regularly modified by mixing the sample with a solid oxidant or activator. Materials added include potassium or lead dichromate, tungsten trioxide, vanadium pentoxide, potassium chlorate, and the oxides of nickel, manganese, iron, or cobalt.

With most organic samples the prime objective is to separate the resultant volatile and nonvolatile products. Halogens may be released from the matrix by oxidation or reduction (e.g., fusion with an alkali metal) prior to being trapped as salts, while inorganic components are left as oxides in dry ashing procedures.

Where one is interested primarily in the inorganic or nonvolatile components, the organic matrix can be destroyed by wet methods, so eliminating the need to risk losses on subsequent dissolution of the residue (which is often refractory) left on dry ashing. However, for extreme trace analysis the procedure recommended is "low temperature ashing". The sample in this case is maintained at a temperature between 100 and 200° and is covered by a low pressure (2 to 5 mm Hg) atmosphere of oxygen. The gas is excited by a high-frequency field, and the resulting atoms effectively destroy complex organic materials with minimum loss of volatile inorganic components.

The range of materials that require dissolution as a preliminary to chemical analysis is almost infinite. Most commercial products are complex and one has to consider possible losses of components due to volatilization, formation of precipitates, etc. In addition, analytical techniques impose restrictions in terms of the nature of the test solution; for example, metal-fluoride complexes (formed through use of hydrofluoric acid) probably will not react with a selected color-forming reagent.

Each case has therefore to be considered on its own merits, and in many situations an oxidation-reduction process is a reasonable initial choice.

IV. GENERAL COMMENTS

From the preceding review it may perhaps be concluded that the number of published analytical applications of heterogenous oxidations and

TABLE 2
Acids Used in Dissolution of Metals and Alloys

Reagent	Metal type	Alloy type – base material
HCl	Active metals (reduction potentials negative with respect to N.H.E.)	Fe, Al, Zn
HBr		
$HClO_4$ (dilute)		Fe
HNO_3		Fe, Al, Zn
H_2SO_4		Fe, Al, Zn, Mg, Ni and Sn
H_3PO_4		W
HNO_3	Noble metals (reduction potentials positive with respect to N.H.E.)	Cu, Sn, Pb
HNO_3 + HCl		Pb and Ni
$HClO_4$ (hot, conc.)		Ni, stainless steel
HF		
HF + HNO_3		Ferro-alloys, Ti, Zr, Hf, Ta, Nb
HF + $HClO_4$		Cr, Mo, W
	Oxidant Fusion Mixtures	
Na_2CO_3 + KNO_3	Ferro-alloys, refractory oxides, sulfides, silicates	
Na_2O_2	Ferro-alloys, chrome ores, refractory oxides, sulfides	
$K_2S_2O_7$	Refractory oxides of Be, Al, Ti, Ta, Zr	
$K_2S_2O_7$ + KHF_2	Minerals containing Nb, Ta, Zr, Be	

TABLE 3
Modes of Dissolution for Organic Compounds

Type	Description	Special applications or comments
Dry ashing	Crucible and flame or furnace	Air-oxidation; residue consists of inorganic species. Some Hg, Cd, Cu, As, and Ag may be lost.
	Tube furnace – oxygen stream	Gaseous products collected; used in determination of major elements
	Low-temperature, "active" oxygen	Low oxygen pressure; volatile elements can be trapped; used for residue analysis
	Oxygen flask	Combustion in O_2, products sorbed in liquid; used for determinations of S, halogens, and metals
	Oxygen bomb	Combustion in oxygen at high pressure (e.g., 20 atm); main application is for determination of S and halogens
	O_2-H_2 flame	Higher temperature decomposes stable compounds
	Lamp method	Liquid burnt in lamp; gases collected for determination of S
Wet ashing	Single acids	HNO_3 (high temp) – biological samples H_2SO_4 + K_2SO_4 + catalyst – Kjeldahl N
	Mixed acids	HNO_3 + $HClO_4$ – protein and carbohydrate HNO_3 + H_2SO_4 – plants $HClO_4$ + HNO_3 + H_2SO_4; universally applicable and is preferred method; allows rapid oxidations of difficult samples
Oxidizing agents	H_2O_2 – H_2SO_4	Powerful; useful for organometallics, plants
	H_2O_2 – HNO_3	Biological samples – rapid for small samples, low temperatures
	H_2O_2 – Fe^{2+}	Ashing occurs through OH-radical formation, and at about 100°. Widely used (except fats, oils, plastics)
	Persulfate	With Ag^+ catalyst oxidizes C to CO_2 for determination of C
	Iodic and chromic acids	In H_2SO_4 – H_3PO_4 solution produces CO_2 for determinations of C in biological materials
	Fuming HNO_3	Closed tube; determinations of S and halogens in volatile organometallics
Fusion	Peroxide bomb (Parr)	Sample burnt in Na_2O_2 containing accelerator (KNO_3, $KClO_3$, or $KClO_4$); used for determinations of S, halogens, P, B, Si, As, and Se
	Alkali metal	Sealed tube; determinations of halogens

reductions is extremely small, that current interest in them is minimal, and hence, with the exception of dissolution procedures, that only limited developments can be expected in the future.

Against this negative view, it may be claimed that a restricting influence in the past has been ignorance of the mechanisms of heterogeneous reactions, and that new specific uses of such systems will follow elucidation of basic reactions. In the field of organic synthesis this tenet seems to apply, and a careful reading of some of the reviews listed[64-67] could provide inspiration for some new methods of functional-group analysis.

The two major limitations of heterogeneous reactions which have to be overcome in quantitative applications are the slow reaction rates and frequent lack of stoichiometry.

With some understanding of potential rate-controlling processes, appreciation of the role of adsorption phenomena, and knowledge of relevant kinetic parameters, these limitations may be overcome. Admittedly, the existing knowledge of mechanisms provides only an indication rather than a detailed guide as to how a system may behave, but this should not deter the keen experimentalist.

There are many unexplored systems and problems (including the reactions of precious metal oxides, specific reductants for organic compounds, oxidations of inorganic species with nickel peroxide, and elucidation of dissolution and reaction mechanisms, etc.), so there is ample scope for research programs.

Further extensions include studies of the redox reactions in flames (relevant to atomic emission and absorption spectrophotometry) or fusion systems.

The effort involved could be justified on the basis of pure research. Or it could be claimed that more should be known about the possible transformations that may be induced by metal oxides present in soils. Alternatively, an analytical chemist may claim that he is preparing for the time when he is required to distinguish between the behavior of different surfaces, or natural minerals, in terms of reactivity rather than total content.

For example, some of the lead said to be polluting our environment is present as the dioxide. Is this more toxic than ionic lead because of the oxidations it can induce, or less important because of its tendency to adsorb sulfur dioxide to form a sparingly soluble salt? If there is a positive answer to this question, analysts should be seeking methods of distinguishing between the chemical forms.

In the past it has been possible to avoid the complexities of heterogeneous redox reactions by employing alternative techniques or by adjusting the experimental conditions on some empirical basis. In the future, adjustments could be more scientifically based and full use made of the positive attributes of heterogeneous systems, which include controlled potential, controlled liberation of reagent, preferential adsorption of some species, and an extended variety of reactions.

Electroanalytical chemists have succeeded in taking full advantage of the phenomena encountered in heterogeneous electron-transfer processes, where there is the additional external stimulus of an applied potential. Are solution chemists willing to accept the same type of challenge?

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REFERENCES

1. Garn, P. D., *CRC Critical Reviews in Analytical Chemistry,* 3, 65 (1972).
2. Delmon, B., Introduction à la kinétique hétérogène, *Collection Science et Technique du Petrole,* No. 15, Technip, Paris, 1969.
3. Sestak, J. and Berggren, G., *Thermochim. Acta,* 3, 1 (1971).
4. Sekerka, I., *Werkstoffe Korrosion,* 10, 383 (1959).
5. Yano, M., Imoto, T., and Moriyama, A., *Kogyo Kagaku Zasshi,* 65, 485 (1962).
6. Moriyama, A., *Kogyo Kagaku Zasshi,* 66, 297, 1289 and 1407 (1963).
7. Teramine, T., Yamamoto, N., and Kawai, M., *Bull. Univ. Osaka Prefect, Ser. A,* 13, 117 (1964).
8. Kawakita, K., *Rev. Phys. Chem. Jap.,* 14, 79 (1940).
9. Chufarov, G. I., Averbukh, B. D., Tatievskaya, E. P., and Antonov, U. K., *Zh. Fiz. Khim.,* 28, 490 (1954); 26, 834 (1952); *Dokl. Akad. Nauk SSSR,* 73, 1209 (1950).
10. McKewan, W. M., *Trans. AIME,* 218, 2 (1960).
11. Seth, B. B. L. and Ross, H. V., *Trans. AIME,* 233, 180 (1965); *Can. Met. Q.,* 5, 315 (1966).
12. Oprya, F. I., *Acad. Rep. Populare Romine, Studii Cercetari Met.,* 5, 203 (1960).
13. Iida, Y. and Shimada, K., *Bull. Chem. Soc. Jap.,* 33, 790 and 1194 (1960).
14. Riddiford, A. C., *Advances in Electrochemistry and Electrochemical Engineering,* Vol. 4, Delahay, P. and Tobias, C. W., Eds., Interscience, New York, 1970, 47 et. seq.
15. Pratt, E. R. and Suskind, S. P., *J. Org. Chem.,* 28, 638 (1963).
16. Pickering, W. F., *Aust. J. Chem.,* 16, 969 (1963); 17, 731 (1964).
17. Steyermark, A., *Quantitative Organic Microanalysis,* 2nd ed., Academic Press, New York, 1961.
18. Svéda, J. and Procke, O., *Chem. Listy,* 19, 163 (1925).
19. Penchev, N. P., *Godishnik Sofuskiya Univ., Fiz. Mat. Fak. Kniga 2–Khim.,* 33, 435 (1935); 49, 53 (1956).
20. King, J. G. and Edgcombe, L. J., Great Britain Dept. Sci. Ind. Research Fuel Research Tech. Paper No. 33 (1931).
21. Mesaric, S., *Croat. Chem. Acta,* 42, 13 (1970).
22. Juracek, M., Cervinka, V., and Cezka, K., *Collect. Czech. Chem. Commun.,* 34, 1162 (1969).
23. Svéda, J., *Chem. Listy,* 19, 41 (1925).
24. Szabó, Z., Soos, I., and Deák, Z., *Z. Anorg. Allg. Chem.,* 252, 201 (1944).
25. Katz, S. H. and Bloomfield, J. J., *Ind. Eng. Chem.,* 14, 304 (1922).
26. Pire, L. R., *An. Soc. Esp. Fis. Quim.,* 27, 192 (1929).
27. Picon, M., *Bull. Soc. Chim. Fr.,* 370 (1956).
28. Wachal, A. L., *Automobile Eng.,* 45, 295 (1955).
29. Milton, R. F. and Waters, W. A., *Methods of Quantitative Micro-analysis,* 2nd ed., Arnold, London, 1955.
30. Fildes, J. E., *Mikrochim Acta,* 978 (1970).
31. Lange, W. and Winzen, W., *Glückauf,* 89, 324 (1953).
32. Pavlyuchenko, M. M. and Rubinchik, Ya. S., *Zh. Prikl. Khim.,* 24, 666 (1951).
33. Bond, W. D., *J. Phys. Chem.,* 66, 1573 (1962).
34. Mire, H., Tokuda, M., and Ohtani, M., *Nippon Kinzoku Gakkaishi,* 34, 814 (1970).
35. Krasuk, J. H. and Smith, J. M., *A.I.C.H.E.J.,* 18, 506 (1972).
36. Mine, T., Suzuki, H., Seiyama, T., and Sakai, W., *Kogyo Kagaku Zasshi,* 64, 1908 (1961).
37. Bransom, S., Hanlon, L., and Smythe, B., *Trans. Faraday Soc.,* 52, 672 (1956).
38. Shurmovskaya, N. A., Bruns, B. P., and Mel'nikova, Z. Ya., *Zh. Fiz. Khim.,* 25, 1306 (1951).
39. Towhidi, N. and Neuschuetz, D., *Arch. Eisenhuettenw.,* 43, 219 (1972).
40. Rotinyan, A. L., *Zh. Prikl. Khim.,* 21, 807 (1948).
41. P'yankov, V. and Drughinin, F., *J. Appl. Chem.,* (U.S.S.R.), 20, 693 (1947).
42. Kolthoff, I. M., Belcher, R., Stenger, V. A., and Matsuyama, G., *Volumetric Analysis,* Vol. III, Interscience, New York, 1957.
43. Clarke, W. E. and Shaw, W. B., *Br. Cast Iron Res. Assoc. J. Res. Develop.,* 6, 512 (1957).
44. Kitagawa, H. and Shibata, N., *Bunseki Kagaku,* 9, 597 (1960).
45. Kitashima, S., *Bull. Inst. Phys. Chem. Res.,* (Tokyo), 7, 1035 (1928).
46. Metzger, F. J., *J. Am. Chem. Soc.,* 31, 523 (1909).
47. Stoner, G. A., *Anal. Chem.,* 27, 1186 (1955).
48. Larsen, R. P., Ross, L. E., and Kessner, G., U.S. Atomic Energy Comm. ANL - 5810 (1957).
49. Kimura, K. and Murakima, Y., *Mikrochimie Ver. Mikrochim. Acta,* 36/37, 727 (1953).
50. Tanaka, M., *Bull. Chem. Soc. Jap.,* 26, 299 (1953); 27, 10 (1954).
51. Lingane, J. J. and Davis, D. G., *Anal. Chim. Acta,* 15, 201 (1956).
52. Tanaka, M., *Bull. Chem. Soc. Jap.,* 23, 165 (1950).
53. Lloyd, C. P., *Anal. Chim. Acta,* 43, 95 (1968).
54. Lyden, R., *Z. Anorg. Allg. Chem.,* 234, 59 (1937).
55. Hans, F., *Z. Anorg. Allg. Chem.,* 140, 337 (1924).
56. Jirsa, F., *Chem. Listy,* 19, 114 (1925).

57. Lloyd, C. P. and Pickering, W. F., *Talanta,* 16, 532 (1969).
58. Terni, A. and Malaguti, P., *Gazz. Chim. Ital.,* 49, 251 (1919).
59. Muller, E. and Messe, W., *Z. Anal. Chem.,* 69, 165 (1926).
60. Peshkova, V. M. and Mel'chakova, N. V., *Metody Analiza Redkikh i Tsvetnykh Metal,* 93 (1956).
61. Deviller, M., *Ann. Pharm. Fr.,* 19, 131 (1961).
62. Ulubelen, A., *Rev. Fac. Sci. Univ. Istanbul, Ser. C.,* 24, 145 (1959).
63. Willard, H. H. and Thomson, J. J., *Ind. Eng. Chem., Anal. Ed.,* 3, 399 (1931).
64. Evans, R. M., *Q. Rev. Lond.,* 13, 61 (1959).
65. Pickering, W. F., *Rev. Pure Appl. Chem.,* 16, 185 (1966).
66. Meth-Cohn, O. and Suschitzky, H., *Chem. Ind.,* (London), 14, 443 (1969).
67. Nakagawa, K., Konaka, R., and Sugita, J., *Shionogi Kenkyusho Nanpo,* 19, 141 (1969); Konaka, R., *Yuki Gosei Kagaku Kyokai Shi,* 30, 479 (1972).
68. Stewart, R., *Oxidation Mechanisms,* Benjamin, New York, 1964.
69. Hodges, R. J. and Pickering, W. F., *Aust. J. Chem.,* 19, 981 (1966).
70. Lloyd, C. P. and Pickering, W. F., *J. Inorg. Nucl. Chem.,* 29, 1907 (1967).
71. Clark, A. J. and Pickering, W. F., *J. Inorg. Nucl. Chem.,* 29, 836 (1967).
72. Drotschmann, C., *Batterien,* 15, 239, (1961) and 20, 911, (1966); *Chem. Weekbl.,* 61, 581, (1965).
73. Koch, D. F. A. and Walkley, A., Trabajos Reunión Internacional Reactividad Solidos, 3, Madrid (1956), 453; *Aust. J. Chem.,* 10, 150 (1957).
74. Gabano, J. P., Etienne, P., and Laurent, J. F., *Electrochim. Acta,* 10, 947, (1965).
75. Nesmeyanova, G. M. and Vikulov, A. I., *Zh. Prikl. Khim.,* 35, 989 (1962).
76. Prasad, M. and Naqui, M. A., *Curr. Sci.,* 8, 361, (1939); *J. Indian Chem. Soc.,* 17, 370 (1940).
77. Zosimovich, D. P., Antonov, S. P., and Gumen, A. S., *Ukr. Khim. Zh.,* 32, 1071 (1966).
78. Gordan, G. and Taube, H., *Inorg. Chem.,* 1, 69 (1962).
79. Lal, K., *J. Indian Chem. Soc.,* 29, 934 (1952).
80. Benes, J. and Uhlir, Z., *Chem. Prum.,* 11, 285 (1961).
81. Pickering, W. F., *Aust. J. Chem.,* 16, 969 (1963); 17, 731 (1964).
82. Lloyd, C. P. and Pickering, W. F., *Talanta,* 11, 1409 (1964).
83. Markidos, A. C. and Hackerman, N., *J. Electrochem. Soc.,* 105, 156 (1958).
84. Vagramyan, A. T., Zhamagortsyan, M. A., Uvarov, L. A., and Yavich, A. A., *Elektrokhimiya,* 6, 755 (1970).
85. Inui, T., Hosokawa, K., and Matsumara, Y., *Kyushu Kogyo Daigaku Hokoku,* 13, 11 (1963).
86. Felloni, L. and Bolognesi, G., *Ann. Chim.* (Rome) 47, 985, (1957).
87. Abramson, M. B. and King, C. V., *J. Am. Chem. Soc.,* 61, 2290 (1939).
88. Gatos, H. C., *J. Electrochem. Soc.,* 103, 286 (1956).
89. Wesley, W. A., *Trans. Inst. Metal Finish.,* 33, 1 (1956).
90. Berenblit, V. M., *Tr. Gos. Inst. Prikl. Khim.,* 44, 108 (1960).
91. Zembura, Z. and Glodzinski, W., *Rocz. Chem.,* 42, 1525 (1968).
92. Gregory, D. P. and Riddiford, A. C., *J. Electrochem. Soc.,* 107, 950 (1960).
93. King, C. V. and Lang, F. S., *J. Electrochem. Soc.,* 99, 295, (1952); Salzberg, H. W. and King, C. V., *J. Electrochem. Soc.,* 97, 290 (1950).
94. Chulanova, G. A., Gorelik, G. N., and Pavdel, A. A., *Zh. Prikl. Khim.,* 45, 517 and 1259 (1972).
95. Borchers, H. and Krug, H., *Werkst. Korros.,* 22, 125 (1971).
96. Goodrich, J. D. and Schmid, C. M., *Corrosion,* 24, 252 (1968).
97. Stephen, W. I., *Ind. Chemist,* 28, 13 (1952); 29, 31, (1953).
98. Yoshimura, C., *J. Chem. Soc. Jap. Pure Chem. Sect.,* 73, 702 and 785 (1952); 74, 544 and 747 (1953).
99. Yoshimura, C., *J. Chem. Soc. Jap. Pure Chem. Sect.,* 75, 603 (1954).
100. Ankudimova, E. V., *Otdel. Khim. Nauk,* 5, 197 (1954).
101. Yoshimura, C., *J. Chem. Soc. Jap. Pure Chem. Sect.,* 76, 409 (1955).
102. Simon, A. C., Miller, P. S., Edwards, J. C., and Clardy, F. B., *Anal. Chem.,* 18, 496 (1946).
103. Norwitz, G. and Codell, M., *Anal. Chim. Acta,* 11, 32 (1954).
104. Fritz, J. S., Fulda, M. O., Margerum, S. L., and Lane, E. I., *Anal. Chim. Acta,* 10, 513 (1954).
105. Cooke, W. D., Hazel, J. F., and McNabb, W. M., *Anal. Chem.,* 22, 654 (1950).
106. Sill, C. W. and Peterson, H. E., *Anal. Chem.,* 24, 1175 (1952).
107. Walden, G. H., Hammett, L. P., and Edmonds, S. M., *J. Am. Chem. Soc.,* 56, 350 (1934).
108. Yoshimura, C., *J. Chem. Soc. Jap. Pure Chem. Sect.,* 73, 362 (1952).
109. Dolezal, J., Drahonovsky, J., and Zyka, J., *Collect. Czech. Chem. Commun.,* 24, 3649 (1959).
110. Miller, C. C. and Chalmers, R. A., *Analyst,* 77, 2 (1952).
111. Pantani, F., *Anal. Chim. Acta,* 31, 121 (1964).
112. Tananaev, I. and Davitaschvili, E., *Z. Anal. Chem.,* 107, 175 (1936); *Zavodskaya Lab.,* 5, 819 (1936); 6, 382 (1937).
113. Yoshimura, C., *J. Chem. Soc. Jap. Pure Chem. Sect.,* 74, 116 (1953).
114. Ishimaru, S. and Saito, K., *J. Chem. Soc. Jap.,* 54, 305 (1951).

115. Yoshimura, C., *J. Chem. Soc. Jap. Pure Chem. Sect.*, 73, 701 (1952).
116. Erdey, L., Buzas, I., and Bodor, E., *Acta Chim. Acad. Sci. Hung.*, 7, 287 (1955).
117. Yoshimaru, C., *J. Chem. Soc. Jap. Pure Chem. Sect.*, 74, 992 (1953).
118. Yoshimaru, C., *J. Chem. Soc. Jap. Pure Chem. Sect.*, 76, 411 (1955).
119. Gowrie, S., Elsie, P., and Shenoi, B. A., *J. Electrochem. Soc. India*, 18, 171 (1969).
120. Riegel, E. R. and Schwartz, R. D., *Anal. Chem.*, 24, 1803 (1952); 26, 410 (1954).
121. De Carvalho, R. A. G., *Anal. Chim. Acta*, 14, 28 (1956).
122. Bryson, A. and Lenzer-Lowry, S., *Analyst*, 78, 299 (1953); 79, 636 (1954).
123. Burriel, F., Lucena-Conde, F., and Bolle, S., *Anal. Chim. Acta*, 9, 293 (1953).
124. Scribner, W. G. and Reilley, C. N., *Anal. Chem.*, 30, 1452 (1958).
125. Cassidy, H. G., *J. Am. Chem. Soc.*, 71, 402 (1949).
126. Manecke, G., *Z. Electrochem.*, 57, 189 (1953); 58, 363 (1954).
127. Repinskii, S. M., *Zh. Fiz. Khim.*, 37, 979 (1963).
128. Owe, T. V., *J. Chim. Phys.*, 54, 169 (1956).
129. Travnicek, E. A. and Weber, J. H., *J. Phys. Chem.*, 65, 235 (1961).
130. Pavdel, A. A. and Gorelik, G. N., *Zh. Prikl. Khim.*, 37, 275, 522 and 577 (1964); *Zh. Vses. Khim. Obshchest.*, 10, 355 (1965).
131. Cretella, M. and Gatos, H. C., *J. Electrochem. Soc.*, 105, 487 (1958).
132. Sata, N., *Nippon Kinzoku Gakkaishi*, 24, 126 (1960).
133. Habashi, F., *Ber. Bunsenges. Physik. Chem.*, 67, 402 (1963).
134. Halpern, J., *J. Electrochem. Soc.*, 100, 421 (1953).
135. Miadokova, M. and Tomkova, M., *Collect. Czech. Chem. Commun.*, 37, 1794 (1972).
136. Deitz, G. A. and Halpern, J., *J. Metals*, 1109 (1953).
137. Filippov, A. A. and Kornakova, S. L., *Sin. Ochistka Anal. Neorg. Mater.*, Tr. Konf. "Nauka-Proizvod" 1965; 148, 156 and 163 (publ. 1971).
138. Willard, H. H. and Rulfs, C. L., in *Treatise on Analytical Chemistry*, Part 1, Vol. 2, Kolthoff, I. M. and Elving, P. J., Eds., Interscience, New York, 1961, Chap. 1, p. 1027.
139. Furman, N. H., *Scott's Standard Methods of Chemical Analysis*, 5th ed., Van Nostrand, New York, 1939.
140. Dolezal, J., Povondra, P., and Sulcek, Z., *Decomposition Techniques in Inorganic Analysis*, Iliffe, London, 1968.
141. Organic Quantitative Analysis, in *Comprehensive Analytical Chemistry*, Vol. 1B, Wilson, C. L. and Wilson, D. W., Eds., Elsevier, Amsterdam, 1960, 399 et. seq.
142. Kuck, J. A., Ed., *Methods in Microanalysis*, Vol. 1-4, Gordon and Breach, New York, 1964.