

Description and Application of Microwave Titrations

Determination of the Reaction Rate and Stoichiometric Composition of Complexes

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► A novel technique allows titrations to be carried out by following the changes in the transmittance curve of a microwave cavity in which a reaction takes place. The inherently simple apparatus has been used for studying the stoichiometric composition and kinetic behavior of donor-acceptor complexes in nonpolar solvents. The construction of the instrument and some applications are discussed. Attractive applications are the determination of aluminum halides in hydrocarbons with ethers, made possible by the formation of strong 1 to 1 complexes, or with 2-propanol with which 1 to 1, 1 to 3, and 1 to 6 complexes are formed. The titrations are characterized by abrupt breaks in the curves, which enable accurate equivalence points to be determined. The isomerization of *n*-propyl bromide with AlBr_3 could be followed quantitatively and formed a valuable addition to our knowledge of this kinetic system.

THE transmission curve of a microwave high- Q resonant cavity is a sensitive function of changes in dielectric matter occupying regions in the electromagnetic field inside the cavity where the electric field strength is large. One of the properties of a microwave cavity inserted in a wave guide system is that it transmits energy only at or near resonance. The expression

$$P(\omega) = \frac{aQ^2P_i}{1 + 4Q^2(\Delta\omega/\omega_0)^2} \quad (1)$$

is a good approximation of the power transmitted as a function of radian frequency (ω). In Equation 1 P_i is the power incident on the cavity, ω_0 its resonant frequency, $\Delta\omega$ the deviation of the actual frequency from ω_0 , and Q a parameter of the cavity, denoted as its quality. The constant of proportionality, a , is related to the degree of coupling of the cavity to the wave guide system. Clearly, Q determines the sharpness of resonance, in that the half-power points on the resonance curve are a distance ω_0/Q apart. When the cavity is constructed with some care, a Q of 4500 at 9000 Mc. per

second is easily attainable, yielding a band width (distance between the half-power points) of 2 Mc. per second.

According to the theory of resonant systems, the physical meaning of Q is that its magnitude is 2π times the ratio of the energy stored in the resonator to the energy dissipated and radiated during one cycle of oscillation. Large Q 's reflect small loss of the energy stored in the cavity, and small additional losses have a considerable effect on the transmission.

In our application these additional losses are caused by the formation of dipoles in a sample inside the cavity in the course of a chemical reaction. The working frequency of 9000 Mc. per second is sufficiently near the critical frequency of most polar substances to cause strong losses whenever dipoles are present.

EXPERIMENTAL

Procedure. The sharpness of resonance of a high- Q cavity, which is necessary to ensure good sensitivity, creates a problem with regard to the frequency stability of the microwave oscillator. The cheapest source of microwaves, a reflex klystron, is not stable enough for measuring the Q of a good cavity; frequency stabilization on another cavity in a discriminator bridge is feasible, but adds considerable instrumental complexity.

Considering that our study was aimed at detecting changes in cavity Q , rather than measuring such changes, we tried very slow frequency modulation of the 2K25 reflex klystron and re-recording of the transmission curve as measured on a detector crystal behind the cavity on a strip chart millivoltmeter. Scanning the transmission curve in this way gives a reproducible record of its maximum height, if a rate of change in frequency can be found which is both fast enough to eliminate erratic frequency drift and slow enough not to exceed the response time of the recorder during passage through the top of the transmission curve. A rate of change of approximately 0.1 Mc. per second was found to meet these conflicting conditions sufficiently to give a

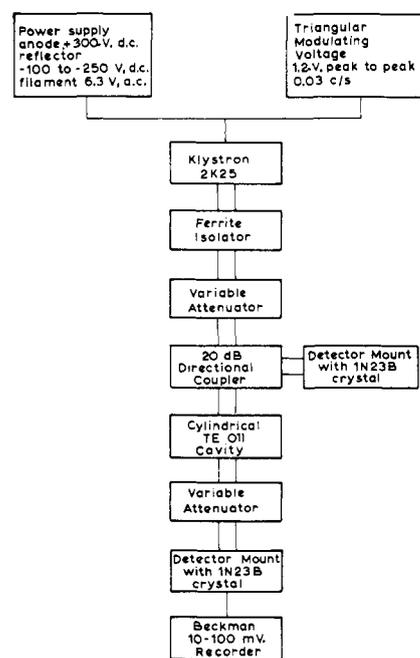


Figure 1. Block diagram of microwave titrator

deflection constant within 0.5% at maximum transmission. Since, according to Equation 1, the maximum value of $P(\omega)$ is proportional to Q^2 , changes of 0.25% in Q may be detected. The frequency of a reflex klystron is modulated by changing the negative potential of one of its electrodes—the reflector. By superposing a triangular voltage of 1.2 volts and 0.03 c.p.s. on the stabilized reflector voltage, the frequency is made to pass through resonance once in 15 seconds under the conditions for the rate of change given above.

A block diagram of the apparatus of the ultimate design is shown in Figure 1. All components, except the reflector power supply, the cavity, and the triangular voltage source, are commercial.

The microwave part of the instrument is constructed from Philips X-Band components. Anode and filament voltages for the klystron are obtained from a Roband Electronics, Ltd., 300-volt 50-ma. regulated power supply, Type

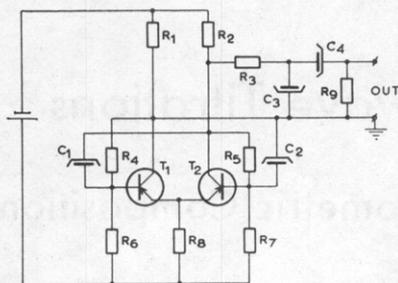


Figure 2. Triangular modulating voltage generator

C_1, C_2, C_4 . 1000 μf .
 C_3 . 2000 μf .
 T_1, T_2 . OC 306/3 (any small high β transistor will work in this circuit)
 R_1, R_2 . 1.8 kilohms
 R_3, R_4, R_5 . 12 kilohms
 R_6, R_7 . 3.9 kilohms
 R_8 . 470 ohms
 R_9 . 27 kilohms

M 33 A. The reflector draws negligible current; its power supply is conventional and consists of a cascaded arrangement of seven 85A2 voltage reference tubes, a series of four tubes supplying stabilized current to another series of three tubes. The resulting voltage stability of 0.06% is amply sufficient for our purpose. The triangular wave form for the slow frequency modulation is generated by a free-running transistor multivibrator, the output of which alternately charges and discharges a large electrolytic condenser. A simplified schematic is given in Figure 2. Obviously, no perfect triangle is generated, the rising and falling slopes being exponential functions of time; however, as long as the rate of change of the frequency at maximum transmission meets the conditions specified above, the deviation from linearity is unimportant.

The cylindrical TE 011 cavity is identical to that used in our electron spin resonance (e.p.r.) spectrometer and is made of silvered wonderstone (3). Cavity Q , when empty, is about 5000.

It might be imagined that the conflicting requirements for the H - and E -field mode patterns for e.p.r. and dielectric measurements would make the use of another type of cavity preferable. In fact, the electric field strength in the axis of a TE 011 cavity is zero, and no effect from a dielectric present there is to be expected.

However, our primary consideration in constructing the apparatus was simplicity and the use of available components. The relative unsuitability of the TE 011 cavity for use in the study of dielectric properties is largely offset by its excellent Q and by the possibility of employing relatively wide sample types. The sensitivity suffices for the investigation of rather dilute solutions in nonpolar solvents. The effect of sample tube diameter on the sensitivity is discussed below.

The function of the microwave com-

ponents not yet discussed is as follows: The ferrite isolator prevents reflected energy from reaching the klystron, which would result in frequency pulling. Its action is supported by the first attenuator, which also establishes an energy level low enough for the detector crystals to work in their quadratic region—i.e., the region where the crystal output voltage is proportional to the incident energy. The directional coupler transfers part of the energy flow in the main wave guide toward the first detector, which monitors klystron operation. The attenuator behind the cavity was included to reduce reflections from the second detector toward the cavity and to control the recorder input further (Figure 3).

The glass part of the apparatus is identical to that described by Adema, Bartelink, and Smidt (2), in an e.p.r. study of Ziegler catalyst systems. It consists of a reaction vessel with a magnetic stirrer, which also serves as a centrifugal pump. The reacting mixture of components passes through a glass or quartz tube placed in the axis of the microwave cavity. The sample tube is rigidly fixed with respect to the cavity by two metal clamps attached to the nearest wave guide flanges. An advantage of the TE 001 cavity for the present application is the simple assembly of the glass components, which facilitates the construction of a hermetically sealed apparatus having no dead corners. The systems investigated are extremely sensitive to moisture, oxygen, and carbon dioxide from the air. The chemical components are introduced into the reactor from nitrogen-filled burets, through magnetically actuated valves. Before the start of a titration, the reactor and tubing are flushed with dry nitrogen at 120° C; see Figure 4.

Table I. ϕ Values of Compounds Dissolved in Heptane as Found in 0.465-Cm. I. D. Borosilicate Glass Measuring Tube at Room Temperature

	ϕ	μ^a
Butyric acid	0.02	0.63
tert-Butyl alcohol	0.13	1.66
Ethanol	0.13	1.68
2-Propanol	0.18	1.68
Cyclohexanol	0.32	1.9
Dibutyl ether	0.33	1.22
Diisopropyl ether	0.35	1.22
Propionaldehyde	0.40	2.57
Acetone	0.48	2.72
Nitromethane	0.61	3.17
Isopropyl bromide	1.46 ^b	2.2
<i>n</i> -Propyl bromide	1.40 ^b , 0.60	2.13
Ethyl bromide	0.60	2.01
Acrolein	1.12	2.88
Acetonitrile	1.19	3.37
Diethyl malonate	1.26	2.54
Cyclohexanone	1.8	2.8
Acetophenone	2.62	2.77
Benzonitrile	4.75	4.05
<i>o</i> -Nitroanisole	9.80	4.81

^a Literature values (15).

^b In carbon disulfide.

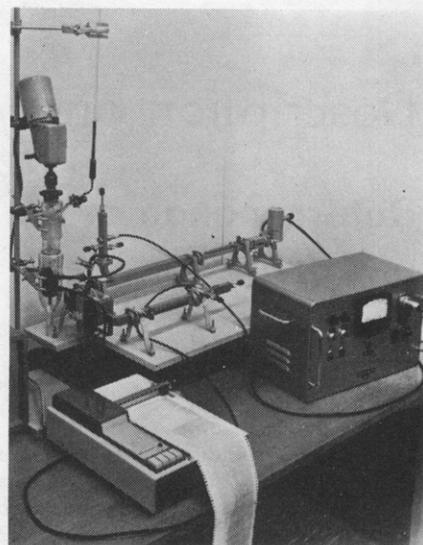


Figure 3. Microwave titrator

RESULTS

The data used in the evaluation of the experimental results are the peak heights in the recorded sequence of transmission curves. Equation 1 shows that these peak heights are proportional to Q^2 if the crystal voltage is proportional to incident energy. The latter requirement is only partly satisfied in our instrument. Factors governing the crystal voltage as a function of incident microwave power level are crystal matching to the wave guide, and individual crystal characteristics, which, again, are a function of temperature and of millivoltmeter impedance. For a servo-recorder, the input impedance is dependent on the deviation of the pen from its equilibrium position. Also, crystal matching is a function of incident power and frequency, which obviously change in the course of a titration.

The precautions we took were matching the crystal as closely as possible at the relevant power level and choosing this level below 10 mv. on the recorder by means of the second attenuator. Even then the supposition that the detector is quadratic is no more than a working hypothesis, which, however, as borne out by the results, cannot be very far beside the truth. In the case of a quadratic crystal the square root of the recorded peak heights is proportional to Q . The reciprocal of Q is a measure of the energy loss inside the cavity. This energy loss is the sum of individual losses, one of which is caused by new molecules formed inside the sample tube. Accordingly, the quantity plotted against concentration or time in the following examples is

$$\Delta \equiv \sqrt{\frac{V_0}{V}} - 1$$

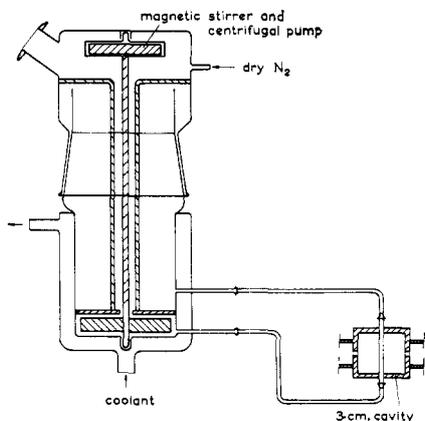


Figure 4. Reaction vessel and measuring cavity

V_0 and V being the initial and subsequent peak heights, respectively, of the recorded transmission curves.

In Figure 5 some Δ 's for the polar compounds indicated are plotted against concentration in heptane solutions. There is usually excellent linearity in concentration at low concentrations. A not very distinct correlation with the dipole moment is evident. The breaks in the curves for acetonitrile and nitromethane are due to limited solubility. The initial slopes of the Δ vs. c plots are summarized in Table I. We introduced the symbol ϕ for $[\Delta/c]_{c \rightarrow 0}$.

Although not substantiated here, it was also found that for a mixture of non-interacting substances in dilute solution Δ equals the sum of the individual Δ values.

The Δ and ϕ values given here are relative values only; any changes in the instrument may give different numerical values which, however, are proportional to those found previously. The extreme ϕ values of the aluminum halide complexes in Table II, which are in good agreement with the large dipole moments of these substances (9, 11, 12), explain the abrupt changes in the slopes of the titration curves discussed below. For some systems the dependence of ϕ on the inner diameter of the sample tube was investigated separately. It was found that ϕ is proportional to the fourth power of the diameter. Variation of the sample tube diameter is a simple means for adapting the sensitivity of the method to the properties of the system investigated. For sparingly soluble compounds titrations below the 1 mmole per liter level could be carried out in wide sample tubes.

LEWIS ACID-BASE TITRATIONS

The titration of AlBr_3 in benzene with di-*n*-butyl ether, illustrated in Figure 6, was carried out by adding about 10 ml. of dilute solution of the ether. There is no evidence of the formation of com-

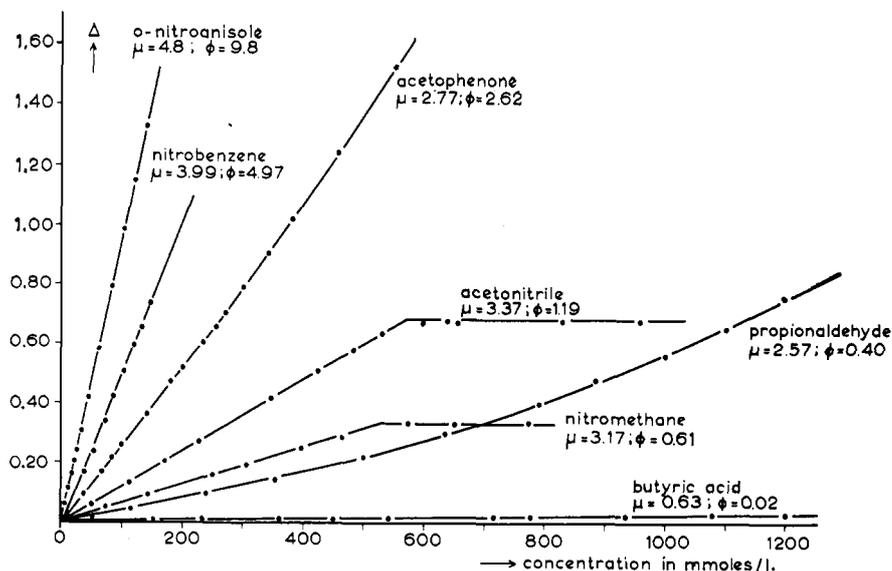


Figure 5. Δ values of some compounds as a function of concentration in heptane at room temperature

pounds other than the 1 to 1 complex. The sharp break in the curve shows that the complex formation is complete; the points in the plot are reached instantaneously on the time scale of the instrument. The ϕ value of the etherate is found to be 31.4, in accord with its large dipole moment.

In 1931 Ulich and Nespital (12) studied a series of donor-acceptor complexes having the general formula $\text{MX}_3 \cdot \text{Y}$ —i.e., $\text{AlCl}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ and $\text{AlBr}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$. They described these complexes as very stable compounds that could not be shown to dissociate into their components. From molecular-weight determinations it appeared that, because of their large dipole moments, these compounds have a tendency to dipole association.

Jacobson and Kraus (4), from con-

ductivity measurements in CH_3Br , found a 1 to 1 addition complex formed from AlBr_3 and $(\text{CH}_3)_2\text{O}$. Since these measurements could be performed only in polar solvents, participation of solvent in the complex formation cannot be excluded. Van Dyke (13), who carried out similar measurements using nitrobenzene as a solvent, found the same result as Jacobson and Kraus. Klages, Meuresch, and Steppich (5) report synthesis of $\text{AlCl}_3 \cdot [\text{diisopropyl ether}]_2$, while Luther, Mootz and Radwitz (6) have given a method for the preparation of $\text{AlCl}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ (m.p. 36°C). Van Dyke and Crawford (14), assuming the equilibrium,

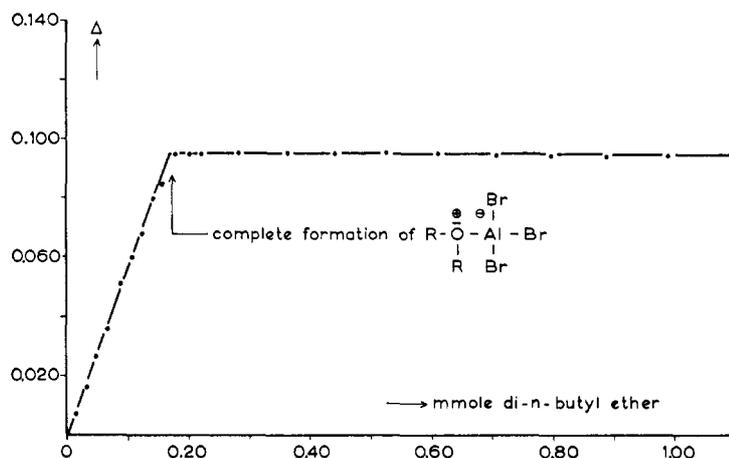
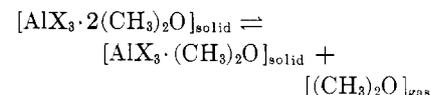


Figure 6. Titration of 0.17 mmole of AlBr_3 in approximately 50 ml. of benzene with di-*n*-butyl ether

Temperature. 20°C .
 $\phi_{\text{compl.}}$ 30.2
 Quartz tube. 0.492-cm. i.d.

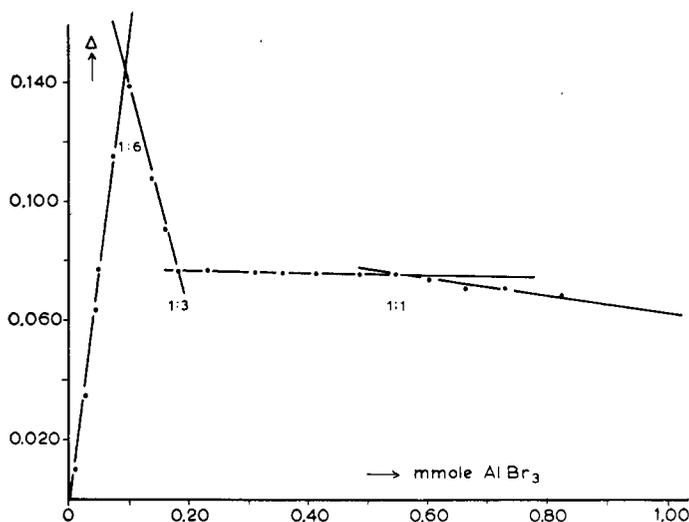


Figure 7. Titration of 0.556 mmole of 2-propanol in approximately 50 ml. of CS₂ with solution of AlBr₃

Quartz tube, 0.492-cm. i.d.

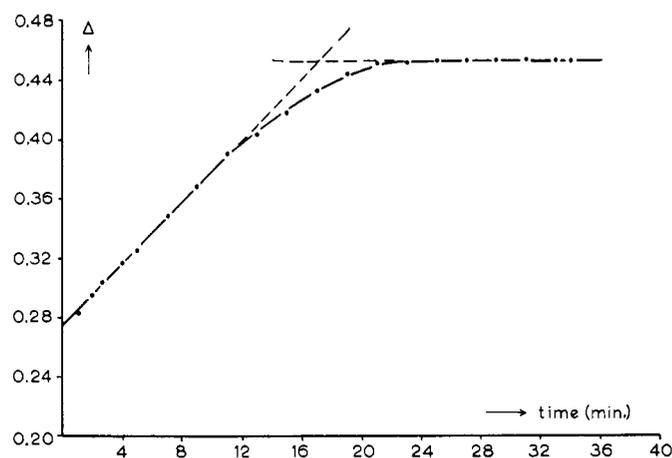


Figure 8. Isomerization of 51.1 mmoles per liter of *n*-propyl bromide to isopropyl bromide in CS₂ under influence of AlBr₃

113.0 mmoles AlBr₃ per liter at 22°C.
Initial rate of isomerization 3.0 mmoles per minute

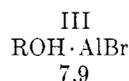
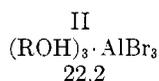
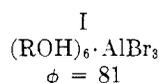
determined the heat of reaction of this system from vapor pressure measurements.

The effectiveness of the present method is shown by the unambiguous insight it gives into the controversial subject of the composition of donor-acceptor complexes with aluminum halides.

Complexes of various alcohols with AlCl₃, having the composition (AlCl₃)_a·(ROH)_b, where *a* = 1 or 2 and *b* = 1, 2,, 10, are described in the literature (10). In view of the high sensitivity of these compounds for oxygen and water, and the techniques used at the time, it is doubtful whether all of the complexes mentioned were indeed present.

When carrying out a titration it is often advantageous to interchange the two solutions. In many cases this has a very distinct effect on the shape of the titration curve.

Figure 7 shows the result of a determination in which 0.084 mole of AlBr₃ per liter was used in titrating 0.556 mmole of 2-propanol dissolved in 50 ml. of CS₂. The position of the breaks indicates formation of complexes having the stoichiometric composition:



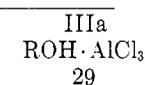
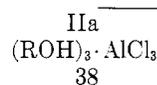
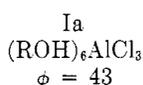
The 1 to 6 complex in particular possesses a very high ϕ value, which suggests the existence of a strongly polarized bond or of ion pairs.

From the sharp break points it must be concluded that the alcohol-aluminum halide complexes are not dissociated. Analogous results are obtained by

Table II. ϕ Values of Complexes Found in 0.492-Cm. I. D. Quartz Measuring Tube at Room Temperature

	Complex	ϕ	Solvent
1:1	AlBr ₃ -di- <i>n</i> -butyl ether	31.4	Benzene
1:1	AlCl ₃ -2-propanol	29	Benzene
1:3	AlCl ₃ -2-propanol	38	Benzene
1:6	AlCl ₃ -2-propanol	43.0	Benzene
1:1	AlBr ₃ -2-propanol	7.9	Carbon disulfide
1:3	AlBr ₃ -2-propanol	22.2	Carbon disulfide
1:6	AlBr ₃ -2-propanol	81.0	Carbon disulfide
1:1	AlBr ₃ -isopropyl bromide	26.0	Carbon disulfide
1:1	AlBr ₃ - <i>n</i> -propyl bromide	17.0	Carbon disulfide

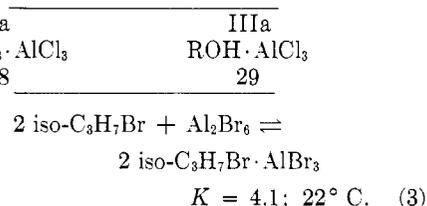
titrating AlCl₃ with 2-propanol in benzene as a solvent. The following complexes are found:



REACTION RATES

The application of the present method is not restricted to the type of titration discussed. It can also be used for following the progress of chemical reactions. The isomerization of *n*-propyl bromide to isopropyl bromide

and that, after complete isomerization ($t = \infty$), it is determined by the equilibrium mixture



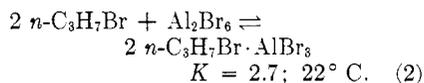
This conclusion was drawn from an extensive investigation of the isomerization at widely varying concentrations of the components (1). Analysis of the data yielded the following values for the components in Reactions 2 and 3.

Compound in CS ₂ (22° C.)	ϕ
Al ₂ Br ₆	0.60
Iso-C ₃ H ₇ Br	1.46
<i>n</i> -C ₃ H ₇ Br	1.40
Iso-C ₃ H ₇ Br · AlBr ₃	24
<i>n</i> -C ₃ H ₇ Br · AlBr ₃	15

It also gave the equilibrium constants of the reactions of Equations 2 and 3. From the initial slope of Figure 8 the rate of isomerization can be deter-

catalyzed by aluminum bromide is illustrated in Figure 8.

It can be shown that initially ($t = 0$) the ϕ value is that of the equilibrium mixture



mined. The kinetic formulation could be explained by means of a plausible mechanism.

CONCLUSIONS

The instrument described has given very good service over one year. Intended as a straightforward extrapolation of the well-known radio frequency titration procedures, its utility has greatly exceeded expectations.

When low cost is not of primary importance, considerably more accurate and sensitive instruments can be constructed according to the same principles. A possible refinement, at the expense of simplicity, is the frequency stabilization of the klystron referred to above. Both heights of transmission curve and tuning of the cavity can then be measured.

A more elegant and simpler approach is to use a varactor microwave source, which generates microwave energy by multiplying, by means of voltage-variable capacitance diodes (8), the frequency of the output of a crystal-

controlled r.f. transistor-oscillator by an exact factor in the order of 200. These rugged all-solid-state devices are capable of furnishing several milliwatts of microwave power at very constant frequency.

Surprisingly accurate and sensitive measurements can be carried out by means of these generators. Using the Microwave Associates MA-8252 B varactor source with an output of 12 mw. at 9000 ± 0.01 Mc. per second it was found that, in a balanced microwave bridge, the d.c. detector output changes by as much as 10 mv. when dry nitrogen is substituted for air inside a 9-mm. i.d. quartz tube in the axis of the microwave cavity.

A more detailed description of the latter instrument and its possibilities will be published in the near future.

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Cation Exchange Separations Using Ammonium Thiocyanate—Organic Solvent—Water Eluants

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► The distribution coefficients of several metals have been measured on Dowex 50-X8 with systems containing various ratios of NH_4SCN , organic solvent, and water. The concentration of organic solvent in a system greatly affects the distribution values. The nature of the organic solvent also has some effect. Most metals have decreasing distribution coefficients with increasing amounts of NH_4SCN in methanol. Several separations were performed using eluting agents suggested by the distribution data.

A WIDE VARIETY of inorganic anions have been used as eluting agents for the separation of metal ions on ion exchange resins. Of these the thiocyanate ion, although utilized to some extent in both anion and cation exchange, has not been systematically studied.

Coleman *et al.* (3) separated rare earths from Am by first removing the metal ions from a cation column with

5M NH_4SCN and passing the effluent into an anion column. Surls and Choppin (14) studied the adsorption of thiocyanate complexes of actinides and lanthanides on anion and cation resins. Using aqueous thiocyanate solutions and anion resin, Teicher and Gordon (15) separated Fe^{+3} and Al and Turner, Philp, and Day (16) separated Cr^{+3} from Sc and Ni and Co from Fe^{+3} . Hamaguchi and workers (6-9) have used aqueous $\text{NH}_4\text{SCN-HCl}$ solutions to separate Sc from a number of metals on anion or cation resins and to study the thiocyanato-chloro complexes of some other metals. Korkisch and Hecht (10) separated Ga from Fe^{+3} on anion resin. These latter two methods depend, in part, on elutions with HCl.

One problem which has limited the use of thiocyanate solutions as an eluting agent is the fact that very large concentrations of thiocyanate salt solutions are often needed to remove many cations from a cation resin or to cause the metal ions to be retained by anion resins. The concentrated solutions are more viscous and difficult to work with. If recovery or analysis of the separated metal is desired, one is faced

with removing or analyzing for the metal ion in presence of large concentrations of thiocyanate salts. In part, this problem has been overcome by employing $\text{NH}_4\text{SCN-HCl}$ mixtures as eluting agent (6-9). Another approach to the problem, which is considered in this report, is the use of an organic solvent mixed with the aqueous thiocyanate salt solution.

Previous work by Fritz and Pietrzyk (4) and others (5, 11, 17) with inorganic anions as eluting agents has shown that the presence of water-miscible organic solvent greatly affects the retention properties of many metals on anion and cation resins through enhanced complex formation. Thus considerably lower concentrations of the complexing agent are required for the separations. It would be expected that thiocyanate complex formation in presence of a water-miscible organic solvent would be enhanced and consequently would have a pronounced effect on exchange separation of metal ions.

The present work describes a systematic study of the sorption of metal ions on strongly acidic cation exchange resins in presence of water-

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