Appendix - A.

Modified method of preparation of cis $\left[^{\text{Coen}_2{(RCO_2)}_2}{\text{ClO}_4}\right]$

Cis $\left[^{\text{Coen}_2{(RCO_2)}_2}{\text{ClO}_4}\right]$ (R = CCl₃, CHCl₂, CH₂Cl) complexes.

In the spectral study of the complexes, Kuroda and Gentile prepared above mentioned complexes by the method of Linhard and Weigl. The method is tedious and lengthy. It was therefore, considered that some modification is necessary in the preparation of these complexes. Details of the present method of preparation are as follows.

Cis $\left[^{\text{Coen}_2{(CCL_3CO_2)}_2}{\text{ClO}_4}\right]$ — The carbonato complex

A mixture of $\left[^{\text{Coen}_2}{\text{CO}_3}\right]$ (2 g.), CCl₃CO₂H (2 g.) and 2 ml of water was evaporated to almost complete dryness at 60 - 65°C. Twenty milliliters of cold dilute perchloric acid was added to the reaction product and the reddish precipitate formed was filtered and washed with diluted perchloric acid, n-propyl alcohol and ether. Yield 1.5 g.

To recrystallize, the perchlorate (1.5 g) was dissolved in 100 ml of 50 percent ethanol-water mixture at 40°C, and after filtration the filtrate was cooled to 0°C. Several drops of concentrated perchloric acid were added to the filtrate and the crystals formed were isolated and washed as in (above). Yield 1.3 g.

Cis $\left[^{\text{Coen}_2{(CHCl_2CO_2)}_2}{\text{ClO}_4}\right]$ — A mixture of $\left[^{\text{Coen}_2}{\text{CO}_3}\right]$ (2 g.), CHCl₂CO₂H (1.6 g.) and water (2 ml) was evaporated until it became tarry (~ 3 ml). The
reaction product was mixed with 20 ml. of dilute perchloric acid, and after several minutes of continuous stirring, the tarry phase yielded a crystalline salmon colored product which was filtered, washed with n-propyl alcohol and ether. Yield 1.5 g.

To crystallize, the perchlorate (1.5 g) was dissolved in 100 ml of very dilute perchloric acid, at 40°, filtered and the filtrate cooled in an ice-bath. Several drops of concentrated perchloric acid were added to effect precipitation. The crystals formed were filtered and washed as above. Yield 1.3 g.

Cis $\text{Coen}_2\text{(CH}_2\text{ClCO}_2)^2\text{ClO}_4$ — Same procedure was adopted as described in the case of bis dichloro acetato complex (starting with 2 g carbonato complex and 1.2 g CH$_2$ClCO$_2$H).

References:—


Appendix - B.

Guggenheim has described a method for finding the rate constant \( k \) for a first order reaction followed by a physical measurement. If times \( t, t_1, t_2, t_3 \) etc. and \( t + \Delta, t_1 + \Delta, t_2 + \Delta \), etc, are selected where \( \Delta \) is a constant increment, then the following equations are true.

\[
(\lambda - \lambda_\infty) = (\lambda_0 - \lambda_\infty) e^{-kt} \quad \ldots \ldots \text{(1)}
\]

\[
(\lambda' - \lambda_\infty) = (\lambda_0 - \lambda_\infty) e^{-k(t + \Delta)} \quad \ldots \ldots \text{(2)}
\]

Where \( \lambda \) and \( \lambda' \) are readings of a suitable physical property at \( t \) and \( t + \Delta \), respectively, and the usual first order equation is written in exponential form. Similar equations would be true for \( t_1 \) and \( t_1 + \Delta \).

Subtracting (1) from (2) gives

\[
(\lambda' - \lambda) = (\lambda_0 - \lambda_\infty) e^{-kt} (1 - e^{-k\Delta}) \quad \ldots \ldots \text{(3)}
\]

Or

\[
\ln(\lambda' - \lambda) = -kt + \ln((\lambda_0 - \lambda_\infty)(1 - e^{-k\Delta}))
\]

Or

\[
\ln(\lambda' - \lambda) = -kt + \text{constant}.
\]

Or

\[
\log(\lambda' - \lambda) = -\frac{kt}{2.303} + \text{constant} \quad \ldots \ldots \text{(4)}
\]

Thus the plot of \( \log(\lambda' - \lambda) \) against time should be a straight line with a slope equal to \(-k/2.303\). Equation (4) thus helps in the evaluation of specific reaction rate, \( k \).
Appendix - C.

The present method of measuring the dielectric constant (say, D) of the liquid depends on the fact that the capacitance of a parallel plate condenser when completely filled with the liquid assumes a value equal to the capacitance of the condenser without the liquid in between the plates of the condenser multiplied by the dielectric constant of the liquid. Thus it is essentially the measurement of the capacitances of the condenser for the above two cases viz. with and without the liquid in between the plates. Here this is achieved by measuring the frequencies of parallel resonance of the condenser with a standard inductance with the help of a Q-Meter. Thus, if $f_0$ is the resonant frequency of the combination of the inductance and the condenser alone and $f_d$ is that of the same combination except that the condenser is filled with the liquid, it can be shown

$$\frac{C_S + DC}{C_S + C} = \left(\frac{f_0}{f_d}\right)^2 \quad \ldots \ldots \ldots \ldots \ldots \ldots (1)$$

Where $C_S$ the stray capacitance associated with the connecting leads of the test capacitance $C$. $C_S$ and $C$ can be found from an auxiliary experiment. The choice of the resonant frequency and hence the choice of the standard inductance is governed by the nature of the liquid. Eq. (1) thus helps evaluation of D.