The parameters were taken from references\(^1\) and\(^2\) and frequencies from\(^4\). There is good agreement between the results of the two force fields except in the value of the N\(=\)F stretching constant, \(f_2\). The angle interaction constant \(\alpha_{xx}^2\) has been found to be equal to \(-0.001869\) \(\text{A}^2\) (cis) and \(-0.003460\) \(\text{A}^2\) (trans) and therefore the FNN angle interaction must be important. This may partly justify the introduction of the trans-interaction term \(k_{12}\) in the UBF of \(\text{trans} N_2F_2\).

The torsional mean-square amplitudes in \(\text{trans}\) must be more than that in cis because of the reciprocal trend of the frequencies. This may be responsible for the large values of the perpendicular mean square amplitudes of N\(=\)N and N\(=\)F bonds in \(\text{trans} N_2F_2\).

One of the authors (K. B. J.) is thankful to the Ministry of Education, Government of India, for the award of a Research Fellowship.

Department of Physics, K. Venkateswarlu.
Kerala University, K. Babu Joseph.
Ernakulam Centre,

3. Sanborn, K. H., \(ibid\), 1:60, 33, 1855.

### Table III

Coriolis coupling coefficients of \(\text{cis}\) and \(\text{trans} N_2F_2\)

<table>
<thead>
<tr>
<th>Coupling</th>
<th>cis</th>
<th>trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_2 \times a_4)</td>
<td>(a_1 \times a_4)</td>
<td>(b_1 \times a_2)</td>
</tr>
<tr>
<td>(\xi^1)</td>
<td>(\xi^2)</td>
<td>(\xi^3)</td>
</tr>
<tr>
<td>(S_1)</td>
<td>(-0.7188)</td>
<td>(-0.3077)</td>
</tr>
<tr>
<td>(S_2)</td>
<td>(-0.3564)</td>
<td>(-0.8215)</td>
</tr>
<tr>
<td>(S_3)</td>
<td>(-0.4721)</td>
<td>(-0.958)</td>
</tr>
<tr>
<td>(S_5)</td>
<td>(-0.3733)</td>
<td>(-0.0106)</td>
</tr>
<tr>
<td>(S_6)</td>
<td>(-0.9201)</td>
<td>(-0.3867)</td>
</tr>
</tbody>
</table>

The dehydration increased with temperature while the dehydrogenation showed a decrease above 400\(^\circ\)C. The catalyst is considered to change from \(p\)-type to \(n\)-type above 400\(^\circ\)C.\(^4\)

The decrease in dehydrogenation may be due to this change. This implies that the rate-determining step involves the \(p\)-character of the catalyst and according to Wolkenstein's model,\(^5\) it must be the desorption of acetone.

Increase in contact time caused the dehydrogenation to pass through a maximum. To explain a similar observation, Upadhye\(^6\) suggested that the attainment of equilibrium for the surface reaction is facilitated when acetone is relatively strongly adsorbed. Increase in contact time increases the partial pressure of acetone and the high temperature makes the catalyst more \(n\)-type; both favourable for acetone adsorption.

At lower temperatures, with increase in contact time no maximum was observed for the dehydrogenation because the conditions are not favourable for equilibrium of the surface reaction to be established. The dehydration increased with increase in temperature and contact time. This would mean that chromia is responsible for dehydrogenation and alumina for dehydration.

The presence of hydrogen with the alcohol increased the dehydrogenation. Acetone and cyclohexane were found to suppress the dehydrogenation, suggesting that the alcohol adsorption is inhibited. The dehydration activity remained unaffected. Water also suppresses dehydrogenation considerably. In low concentrations, water increases the dehydration, probably by increasing the surface hydroxyl groups. Pyridine suppresses the dehydration activity showing that the surface acidity is important for dehydration. The dehydration was not completely suppressed suggesting that even weakly acidic areas are enough for the dehydration. Unlike sodium\(^7\) pyridine does not affect the

### DUAL ACTIVITY OF CHROMIA-ALUMINA IN THE DECOMPOSITION OF ISOPROPANOL

The dehydrogenation and dehydrogenation activities of chromia-alumina catalysts have been investigated by many workers.\(^1\)\(^,\)\(^2\) The present study is an attempt to understand the mechanism of the decomposition of isopropanol on chromia-alumina. The effect of contact time and partial pressures was studied using a flow type reactor described by Pandao.\(^3\)
electronic nature of the catalyst and so does not increase the dehydrogenation.

When an equimolar mixture of acetone and hydrogen is sent over the catalyst at 412° C., the gaseous products contained isobutylene, propylene and hydrogen showing that acetone and hydrogen react to form isopropanol. Below 400° C. there was negligible reaction suggesting that an n-type surface favours the reaction. This confirms the conclusions drawn earlier that on a p-type catalyst, the desorption of acetone which is the rate-determining step is facilitated and the equilibrium for the surface reaction is not established. It is concluded that acetone during its adsorption retards dehydrogenation by reducing the donor nature of the catalyst thus preventing the alcohol from getting adsorbed, while hydrogen favours dehydrogenation by increasing the donor nature.

It may be considered that dehydrogenation is greatly affected by the chemisorption of substrates that affect the electronic character of the catalyst, while the dehydration depends only on the surface acidity and is affected only by bases neutralising the acidity. The rate-determining step for the dehydrogenation changes as the electronic nature of the catalyst changes, either due to the temperature or chemisorption of other substrates.

Department of Chemistry, C. Daniel.
Indian Inst. of Technology, J. C. Kuriacose.

Reagents and Apparatus.—An alcoholic solution (0.05 M; containing 12.8 mg. of reagent per ml.) of the reagent was used. Uranyl nitrate solution (0.01 M) was prepared from uranyl nitrate hexahydrate and its uranium content checked up by estimation by the oxine method. Acetate buffer of pH 6.5 was prepared from 1.0 M acetic acid and 1.0 M sodium acetate. 3.0 M KCl solution and 0.01% aqueous solution of thymol were employed as supporting electrolyte and maximum suppressor respectively.

Dr. Lange’s polarometer, Model-3, a direct reading instrument coupled with a multiflex galvanometer (Type MGF 2) and Elico (L 1-10) pH meter were used for current voltage and pH measurements respectively. An H-cell of the type designed by Lingane and Laitinen2 was used both for polarographic and amperometric studies.

Uranyl ions yielded a well-defined polarogram in acetate buffer with E4 at -0.33 v (vs. SCE) with a diffusion plateau ranging from -0.5 v to -0.8 v (vs. SCE). The titrations were performed at an applied potential of -0.5 v, at which potential only uranyl ions yielded diffusion current whereas the reagent requires higher potential for the reduction. The concentration of acetate ion was maintained at 0.05 M in all the experiments to minimise the complicating effect on uranyl ions.

Estimation of uranium.—Known volumes of uranyl nitrate solution (containing ca. 2.0 to 14.0 mg. of uranium) were pipetted out into a 50 ml. volumetric flask. 2.5 ml. of acetate buffer, 7.5 ml. of KCl, 1.0 ml. of thymol solution were added and the solution made up to 50 ml. with water. The solution was transferred into the wider limb of the H-cell and purified hydrogen gas was bubbled through the solution for about 15 minutes to expel dissolved oxygen. The dropping mercury electrode was then placed in solution and drop time adjusted to 2-3 seconds. The applied voltage was set at -0.5 v (vs. SCE). The standard solution of the reagent was added from a micro burette (5.0 ml.). After each addition hydrogen gas was bubbled to mix the solutions. Current values were noted two minutes after stopping the hydrogen gas. Volume correction was applied to each of the current values recorded and plotted against the volume of the reagent added. The equivalence point was located by extrapolating the two branches of the curve. From the amount of reagent consumed by a definite amount of uranyl ions, the

AMPEROMETRIC ESTIMATION OF URANIUM WITH 2', 3', 4'-TRIHYDROXY CHALCONE

The author reported that 2', 3', 4'-trihydroxy chalcone yielded an orange-red precipitate with UO₄²⁻ ions at pH 5.9 to 8.4.¹ Since the reagent gave a well-defined polarographic wave at pH 6.1 in an acetate buffer with E₄ at -1.155 v (Vs. SCE), the reaction was investigated for the amperometric estimation of uranium.