NOTES.

The Reduction of Uranium Hexafluoride with Hydrogen. By J. K. Dawson, D. W. Ingram, and L. L. Bircumshaw.

The extreme reactivity of uranium hexafluoride towards organic compounds is well known (Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XII, Longmans, Green & Co.), these compounds undergoing various reactions involving the substitution of fluorine for hydrogen and the breaking of C–H bonds, whilst the uranium hexafluoride is reduced to the tetrafluoride. There is only one reference in the literature, however, to the reduction of the hexafluoride with gaseous hydrogen : Ruff and Heinzelmann (*Z. anorg. Chem.*, 1911, **72**, 82) record its immediate reduction to the tetrafluoride at room temperature. No further observations on this reaction appear to have been published, but in 1943 H. J. Spencer-Palmer (private communication) described experiments in which he treated the hexafluoride with hydrogen in various vessels at temperatures between $-78°$ and $100°$ for periods of several hours: as catalysts he tried water (vapour) and technical uranium tetrafluoride; in no case was reduction observed.

From these considerations it appeared probable that the materials used by Ruff and Heinzelmann contained an impurity which acted as a catalyst, although it was difficult to see what this impurity could be since it should be presumably volatile enough to distil with the hexafluoride and also, according to Spencer-Palmer, it was not water or any of the products formed by the reactions between the hexafluoride, water, and glass. In an attempt to confirm Spencer-Palmer's work we investigated the conditions under which the reaction takes place.

The equilibrium constant of the reaction

$$UF_{6(g)} + H_2 = UF_{4(s)} + 2HF \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

may be calculated from available thermochemical data, *viz.* :

$$UF_{6(g)} = U + 3F_2 - 505 \text{ kcals.}$$
$$UF_{4(s)} = U + 2F_2 - 446 \text{ kcals.}$$

heat of formation of hydrogen fluoride, $\Delta H_{298} = -69{\cdot}8$ kcals.

The relevant entropy values are :

$UF_6 \; S^0_{298} = 54{\cdot}45$ cals. mole^{-1}deg.$^{-1}$.
$UF_4 \; S^0_{298} = 36{\cdot}12$,, ,,
$HF \; S^0_{298} = 41{\cdot}53$,, ,,
$H_2 \; S^0_{298} = 31{\cdot}23$,, ,,

Hence ΔS^0_{298} for the reaction $UF_6 + H_2 = UF_4 + 2HF = 33{\cdot}5$ cals., and from the relation $\Delta G^0_{298} = \Delta H^0_{298} - T\Delta S^0_{298}$, $\Delta G^0_{298} = -79{\cdot}78$ cals. Then, by applying the well-known equation $\Delta G^0 = -\boldsymbol{R}T \ln K_p$, $K_p = 10^{58}$ at 25°; thus on theoretical grounds the equilibrium is well over to the right-hand side of equation (1) and if attained would lead to complete reaction.

A similar calculation for the reaction $UF_4 + 2H_2 = U + 4HF$ proves that in this case at 25° the equilibrium lies well to the left-hand side, but this is reversed in the region of 1000°.

These theoretical considerations accord with Ruff and Heinzelmann's results but we have been unable to confirm them experimentally.

Experimental.—The method used was to condense, at liquid-air temperatures, a small quantity of uranium hexafluoride in a weighed Pyrex tube which was of known volume to a point marked on a constriction and was attached to a vacuum manifold. The tube was then filled with pure hydrogen (dried over phosphoric oxide), sealed at the mark, and weighed. The weight, corrected for the weight of the air originally present and also for the hydrogen present at the second weighing, gave the weight of the hexafluoride. The tubes were placed in a furnace at a known temperature for the required time and were later broken in water containing a known excess of standard potassium dichromate solution which was then back-titrated with standard ferrous ammonium sulphate solution, tri-*o*-phenanthroline ferrous sulphate being used as indicator. The weight of the tetrafluoride formed was thus determined.

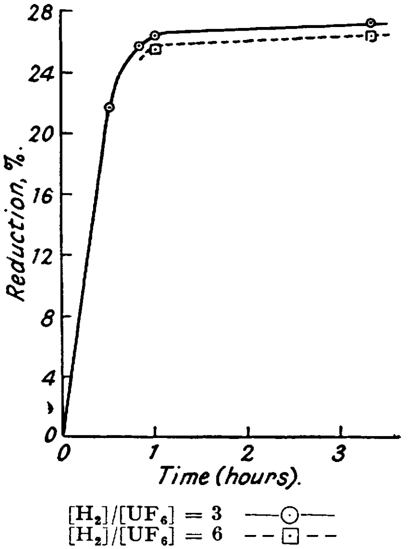
The effect of temperature was first investigated; initially the reaction time was 3 hours. The results at each temperature, although usually in close agreement, sometimes showed divergences outside the experimental limits of analysis. An excess of hydrogen was always used, the actual concentration being independent of the size of the bulb and depending only on the temperature and pressure during sealing off. In experiments at 430°, a reaction occurred in addition to the reduction of the hexafluoride, producing a purple deposit on the walls of the tube instead of the usual dark green of the tetrafluoride. In order to simplify the investigation experiments were therefore confined to temperatures below 350°, the purple compound then not being formed.

The effect of temperature is shown in the table. The reaction time was 30 minutes and the initial concentration ratio, $H_2 : UF_6$, was approx. 5·0 : 1.

Temp., °	226	250	275	285	292
% Reduction	3·8	22·3	40·1	42·5	44·3
Temp., °	295	305	312	330	331
% Reduction	44·8	50·5	52·2	58·6	59·1

The effect of time is shown in the figure. The temperature was 250° and two different ratios of $H_2 : UF_6$ were used, *viz.*, 3·0 : 1 and 6·0 : 1. The results show that a large amount of the reduction takes place in the first 30 minutes. Experiments were made to investigate the kinetics of the reaction. Evidence was obtained for a homogeneous reaction in the gaseous phase, of first order with respect to each reactant, and also a heterogeneous reaction on the wall of the containing vessel. The results, however, were not conclusive and are not included.

Reduction of UF_6 *in a closed system. Temp.* 249—250°.



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Some Reactions of 5-*Nitro*peri*naphthindane*-1 : 2 : 3-*trione Hydrate.* By Radwan Moubasher and Aly Sina.

The preparation and properties of *peri*naphthindane-1 : 2 : 3-trione * have been described by Moubasher and Awad (*J.*, 1949, 1137). We have now prepared the 5-*nitro*-derivative, m. p. 215° (decomp. to a deep red melt) (Found: C, 61·0; H, 2·1; N, 5·9. $C_{13}H_5O_5N$ requires C, 61·1; H, 1·9; N, 5·5%), in the same way, and find that in its solvent properties, its reactivity towards bases [*e.g.*, aniline gives 5-*nitro*-2-*anilino*-2-*hydroxy*peri*naphthindane*-1 : 3-*dione*, m. p. 267° (decomp.) (Found: C, 65·5; H, 3·7; N, 8·1. $C_{19}H_{12}O_5N_2$ requires C, 65·5; H, 3·4; N, 8·0%)], and its reaction with α-amino-acids it closely resembles the parent compound. In addition we have examined its action on ascorbic acid and dihydroxymaleic acid, and have isolated 5-nitro-2 : 3-dihydroxy 1-keto*peri*naphthindene from the reaction mixture.—Fouad I University, Cairo, Egypt. [*Received, August 25th,* 1949.]

* Better named as perinaphthane-1 : 2 : 3-trione. Ed.

Aldehydes from Benzylamines and Isatin. By Alexander Schönberg and Radwan Moubasher.

Schönberg, Moubasher, and Mostafa (*J.*, 1948, 178) suggested that the conversion of, *e.g.*, benzylamine into benzaldehyde by isatin (Traube and Engelhardt, *Ber.*, 1911, **44**, 3148) proceeds by condensation to the Schiff's base, followed by prototropic rearrangement ($\cdot CO\cdot C{:}N\cdot CH_2Ph \longrightarrow \cdot C(OH){:}C\cdot N{:}CHPh$) and hydrolysis. Angyal, Morris, Rassack, and Waterer (*J.*, 1949, 2704) showed that the reaction did not occur with 2 : 4 : 6-trimethyl- or 2 : 6-dichloro-benzylamine and objected to the mechanism just mentioned on the grounds that it should not be subject to steric hindrance. This objection is not valid, for whilst steric hindrance should not affect the prototropic rearrangement it should and does affect the formation of the Schiff's base.

We have confirmed that the starting materials are recovered unchanged after isatin (1 g.) and 2 : 6-dichlorobenzylamine (0·5 g.) have been heated under reflux in water (100 c.c.) for 1 hour.—Fouad I University, Cairo, Egypt. [*Received, February 23rd,* 1950.]