TABLE I. The energy difference between rotational isomers in liquid perfluoro n-paraffins.

Compound	Line pair(s), cm^{-1}	Temperature range, °K	Energy difference cal. mole^{-1}, $-\Delta H$
$n-C_5F_{12}$	834–881	150–220	460±100
	990–1022	150–220	350±150
$n-C_6F_{14}$	795–818	195–280	600±150
	818–833	195–280	580±150
$n-C_7F_{16}$	1030–1058	220–330	600±100

However, the similarity of the vapor and liquid spectra at comparable temperatures shows that the different rotational isomers are present in nearly the same relative concentration in the two phases. We believe therefore that the energy differences in the vapor phase will not be significantly higher than those obtained in this investigation.

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The Variation of Rate of Desorption with Extent of Surface Coverage

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RECENTLY Rideal and Trapnell[1] reported results on adsorption heats which lead to the conclusion that whereas dilute films of hydrogen on tungsten evaporate very slowly, more concentrated films evaporate much more rapidly. This effect is due to the repulsive forces acting between adsorbed molecules, and has an important bearing on the mechanism of the para-orthohydrogen conversion and many other reactions. In connection with a study of the catalyzed ammonia-deuterium exchange reaction, using the technique of microwave spectroscopy to determine NH_3 concentrations, we have recently demonstrated directly that rates of desorption are markedly increased as the surface becomes more fully covered.

The work has been done with a singly promoted iron catalyst (No. 631) kindly supplied by Dr. P. H. Emmett. We have found that the rate of evaporation of deuterated ammonia from the surface is increased markedly as the pressure of NH_3 in the gas phase is increased. For example, with 40 g of catalyst at 122°C and a pressure of 1μ the rate of desorption of deuterated ammonia is 5×10^{-9} mole sec.$^{-1}$. With a NH_3 pressure of 20 cm on the other hand, the rate of desorption is 1.4×10^{-6} mole sec.$^{-1}$; in a 2-liter vessel deuterated ammonia corresponding to a pressure of 1 cm is in fact desorbed in less than 10 min. In view of the effect it is not sufficient, before starting a new experiment, merely to pump out the reaction vessel: the catalyst must be washed several times with the gas mixture to be employed in the experiment.

The effect was first noticed by us on the walls of the 1-cm copper wave guide used. Since the adsorption on an untreated wave guide was sufficient to interfere with the analysis, it was coated with a layer of Glyptal which was then baked; the coating thickness was 0.0003 in. If NH_3 is introduced into such a wave guide and the system then pumped down to 10^{-4} mm, the desorption can be followed both by observation of the increase of pressure and of the pressure broadening of the 3–3 line of the ammonia inversion spectrum. Under these conditions the initial pressure rise is about 5μ per minute. On adding a mixture of NH_3 and deuterated ammonias the rate of desorption of NH_3 can be followed by measuring the total pressure and the peak absorption of the 3–3 line, this peak being approximately proportional to the mole fraction of NH_3. In this way we have found, for example, that a pressure of 0.4 mm increases the rate of desorption of NH_3 by a factor of at least 100. The desorption of deuterated ammonia is found to be similarly increased. In order to analyze mixtures of the ammonias we have therefore found it necessary to wash several times with the mixture to be analyzed.

These results, like those of Rideal and Trapnell, cannot be explained on the basis of variability of the catalyst surface, but only in terms of repulsive forces. Since the rates of catalyzed reactions are sometimes controlled by desorption rates it follows that surfaces may be rendered more active catalytically by the adsorption of reactant or other molecules.

Further details of this work will be included in a later paper on the kinetics of the ammonia-deuterium exchange.

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The Magnetic Susceptibility of Europium and Samarium Amalgam

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THE difficulties encountered in preparing the rare-earth metals have seriously hampered the investigation of the physical and chemical properties of these substances.[1] By far the most extensive piece of work is that of Klemm and Bommer.[2] These investigators prepared the metals by reducing the anhydrous trichlorides with the stoichiometric amount of potassium. We are reporting the results of some preliminary studies of the magnetochemical properties of the rare-earth amalgams. While the literature contains many references to the magnetochemical properties of amalgams,[3] particularly those of the alkali metals, it appears that this approach to the study of the rare-earth metals has been overlooked. Samarium and europium were chosen as the first objects of study because of the considerable theoretical importance attaching to their position near the middle of the lanthanide series.

The origin and purity of the europium used in this research has been discussed in a previous publication.[4] The samarium was obtained from Research Chemicals, Inc.,[5] and was reported by them to be better than 99 percent Sm_2O_3. Purification of the mercury was effected by the usual acid washing and a single distillation. The magnetic susceptibilities of the samarium and mercury were determined in order to establish their purity as regards paramagnetic or ferromagnetic substances. A solution of $SmCl_3$ in dilute HCl was used for the samarium measurement; and the result obtained was $\chi_{Sm}=6.75\pm0.07\times10^{-6}$ c.g.s./g at 27.5°C, in good agreement with Sugden and Tailby's recent determination.[6] The specific susceptibility of mercury was found to be $-0.166\pm0.001\times10^{-6}$ c.g.s./g, agreeing well with the best values from the literature.[7,8]

The amalgams were prepared by reducing the rare-earth acetates in solution with sodium amalgam.[9] After washing with water to remove any unreacted sodium the amalgams were introduced into the sample tubes under dry nitrogen. The susceptibilities were

TABLE I. Magnetic susceptibility of europium amalgam.

Exp't. No.	(1) Force (mg)	(2) Field (oersteds)	(3) Temp. (°C)	(4) Wt. % Eu	(5) $\kappa_{obs} \times 10^6$ (c.g.s./ml)	(6) $\chi_{obs} \times 10^6$ (c.g.s./g)	(7) $\chi_M \times 10^6$ (c.g.s./mole)	(8) μ_{eff}
1	3.9 — 3.4	9104 — 8580	25.0±0.1	0.104	0.47 — 0.48	0.035	29.200 ±1100	8.4±0.2
2	3.3 0.9	9140 8680	25.0±0.1	0.104	0.40 — 0.40	0.030	28600 ±1100	8.3±0.2
3	−19.4	9140	25±1	6.15×10^{-3}	−2.07	−0.154	30400 ±7500	8.5±1.0
4	50.0 — 43.9	9140 — 8680	25.8±0.2	0.307	5.18 — 5.25	0.386	27300 ±200	8.09±9.03
5	48.4 — 42.6	9140 — 8680	25.1±0.2	0.307	5.19 — 5.20	0.385	27200 ±200	8.08±0.03

TABLE II. Magnetic susceptibility of samarium amalgam.

Exp't. No.	(1) Force (mg)	(2) Field (oersteds)	(3) Temp. (°C)	(4) Wt. % Sm	(5) $\kappa_{obs} \times 10^6$ (c.g.s./ml)	(6) $\chi_{obs} \times 10^6$ (c.g.s./g)	(7) $\chi_M \times 10^6$ (c.g.s./ml)	(8) μ_{eff}
1	−15.9	9140	25.0±0.1	0.323	−1.55	−0.115		
2	−14.3	9140	25.0±0.1	0.375	−1.51	−0.112	2360±140	2.38±0.07
							2160±120	2.28±0.06
3	−14.2 — −12.4	9140 8580	24±0.5	0.426	−1.38 — −1.39	−0.102	2250±90	2.32±0.05
4	−11.3 — −10.1	9140 — 8580	25±0.5	0.528	−1.19 — −1.19	−0.088₂	2220±90	2.31±0.05

measured by the Gouy method, the balance used having been described in a previous publication.[10] Analyses were carried out by extracting the rare-earth with warm 6N HCl, precipitating it as the oxalate and igniting to the oxide at 850°C. Precautions were taken during the weighings to prevent appreciable reaction of the oxide with the water and carbon dioxide in the air.

The results of the measurements with europium and samarium amalgams are given in Table I and Table II, respectively. Columns 1 to 5 list the observed quantities as indicated. In calculating the specific susceptibilities (column 6) the density of mercury at the indicated temperature was used. The validity of Wiedemann's additivity law was assumed in calculating the molar susceptibility of the rare-earth component.[11] Effective Bohr magneton numbers (μ_{eff}) are tabulated in column 8 only as a convenient method of comparing observed and theoretical susceptibilities.[12] A diamagnetic correction of -30×10^{-6} c.g.s./mole was applied to the samarium values. The errors indicated are the maximum errors, not probable errors.

Klemm and Bommer found an effective moment of 8.3 for metallic europium.[2] Our result, probably somewhat more accurate, is in good agreement with this. Spectroscopic evidence assigns a configuration (outer shells only) and term symbol to europium of $4f^7 5s^2 5p^6 6s^2 \ ^8S$, for which is calculated an effective moment[13] of 7.94. Thus the magnetic and spectroscopic results are in excellent agreement.

For the case of samarium no such agreement is to be found. At 20°C Klemm and Bommer determined the effective moment of the metal to be 2.07. Our value for the amalgam, namely, 2.28 to 2.38, is definitely greater than that found by Klemm and Bommer for the presumably pure metal. Selwood[14] has measured the susceptibilities of samarium (II) and samarium (III) compounds and reports the following effective moments: Sm(II)=3.62; Sm(III) =1.55. These values for the compounds have been put on a firm theoretical basis by Van Vleck and Frank.[15,16] Any satisfactory explanation of the anomalous moments found for metallic sa-

marium and for its amalgam must await further experimental and theoretical work.

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Carrier-Free Radioisotopes from Cyclotron Targets XI. Preparation and Isolation of Os¹⁸⁵ and Re¹⁸³, ¹⁸⁴ from Tungsten*

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L ONG-LIVED radioisotopes[1] of rhenium and osmium have been isolated in the carrier-free state from a tungsten exit strip which was removed from the 60-in. cyclotron at Crocker