only slightly, if at all, diminished. Similar results have been obtained with preparations from other sources.

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RECEIVED AUGUST 2, 1934

THERMAL DIFFUSION OF GASES NEAR A HOT METAL SURFACE

Sir:

In an experimental study of the equilibrium of molten iron and steam [THIS JOURNAL, **55**, 3131 (1933)] the only criterion of equilibrium was the fact that the oxygen content of the iron reached a constant and reproducible value at a constant steam–hydrogen ratio. The surprising results of Emmett and Shultz [*ibid.*, **55**, 1376 (1933)], in which a thermal separation of steam and hydrogen was observed even in a flowing system, raised the question as to whether such a phenomenon could have occurred in our experiments. This suspicion was heightened by the fact that for a given oxygen content of the liquid iron the observed ratio of steam to hydrogen was consistently a little higher than that calculated from the ratio CO_2:CO found by Vacher and Hamilton [*Trans. Am. Inst. Mining Met. Eng.*, **95**, 124 (1931)].

It should be possible to diminish the temperature gradient and thereby also the amount of thermal separation by preheating the gas stream as it approaches the hot metal surface. The preheating due to radiation from the liquid iron will be the more efficient the lower the lineal velocity of the gases. In the earlier experiments the gases were introduced through a 3-mm. tube at 250 to 450 cc. per minute, whereas Vacher [*Bur. Standards J. Res.*, **11**, 541 (1933)], using a larger tube and lower rate of flow, obtained a lower ratio of steam to hydrogen.

A series of experiments has been conducted in which the steam–hydrogen mixture was admitted through a 7-mm. tube containing an electrically heated spiral of platinum wire. In another series this preheating was supplemented by a cast chromium sleeve which fitted over the top of the crucible containing the melt and which was heated by induction to a temperature approximating that of the liquid iron. The results of these experiments at 1600° and 0.065% oxygen in the liquid iron are given in Table I. The temperature recorded for the platinum coil is its average determined by its resistance. The end nearest the exit was several hundred degrees hotter. The recorded sleeve temperatures are estimates.

TABLE I

THE EQUILIBRIUM: FeO (IN Fe) + H_2 = Fe(l) + H_2O AT 1600°

Expt.	$\frac{p_{H_2O}}{p_{H_2} \times \%O}$	Flow cc./min.	Coil temp., °C.	Conditions
1–18	4.75	300	..	3-mm. tube
33	4.58	300	..	7-mm. tube
34	4.33	300	1170	No sleeve
35	4.23	300	1320	No sleeve
51	4.20	300	1170	Sleeve about 1500°
52	4.04	300	1170	Sleeve about 1600°
53	3.94	200	1170	Same as 52
55	4.20	450	1050	No sleeve

The results substantiate the hypothesis of partial thermal separation of the cold gases near the hot metal surface, which results in a diffusion of steam away from the surface and a low oxygen content of the liquid iron. In experiments 52 and 53 the preheating is believed to have been sufficient to largely eliminate this source of error. These two experiments are also in very good agreement with calculations from similar data on the system Fe:C:O.

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RECEIVED AUGUST 9, 1934

MAGNETIC SUSCEPTIBILITY OF METAL KETYLS

Sir:

We have recently made an investigation on the magnetic susceptibilities of some of the metal ketyls in solution by the Gouy method. The root mean square permanent magnetic moment per molecule was calculated from the molal susceptibility χ_M of the solute by means of the Langevin relation

$$\mu = 2.83\sqrt{T(\chi_M - N\alpha)}$$

μ being in Bohr magnetons. The values of $N\alpha$ were found by Pascal's rule from values in the "International Critical Tables." The percentage dissociation of the metal ketyls under the conditions given in the table below was calculated from the relation

$$D = 100\,(\mu^2/3)$$

which follows from the assumption that the radicals have a magnetic moment of $\sqrt{3}$ Bohr magnetons.

Metal ketyl	Solvent	Concn., wt. %	Temp., °C.	Molal susceptibility of solute, χ_M	D, %
p-Biphenyl phenylketone sodium	Benzene	9.4	27	-152×10^{-6}	1.7
p-Biphenyl phenylketone sodium	Dioxane	3.0	26	+339	41
Benzophenone sodium	Benzene	1.7	25	−195	<1.0

A result for *p*-methoxybenzophenone sodium of $D = 33\%$ at 25° and a concentration of 1.0% with benzene as the solvent was also obtained, but, because of the fact that only a small concentration of the metal ketyl could be obtained coupled with the fact that a relatively large excess of the ketone was necessary to cause reaction with the sodium, a large correction thus being made necessary, the results were considered to be not very significant. We found that α-naphthyl phenyl ketone would not form a metal ketyl in benzene solution even though sodium, potassium and sodium amalgam were tried.

Schlenk and Thal [*Ber.*, **46**, 2840 (1913)] advance as evidence that the metal ketyls are completely dissociated (at least in ether solution) the results of certain boiling point measurements. The boiling point reading of the thermometer was taken first for the pure solvent, then after the addition of a small amount of *p*-biphenyl phenyl ketone, and finally after the addition of some potassium metal. The solution was kept in contact with an atmosphere of nitrogen. Schlenk and Thal state that they observed no fall in boiling point after the addition of the potassium. We have repeated their work as nearly as possible, but have obtained quite different results. We made two runs, in each of which there was a fall in boiling point after the addition of the potassium of approximately one-half of the total rise caused by the addition of the ketone. The fall took place over a period of about an hour, and the final reading was a steady one. The fall in boiling point indicates a decrease in the number of moles of dissolved material; this decrease presumably corresponds to the formation of undissociated molecules of the sodium salt of the pinacol. We attempted the experiment also with dioxane as the solvent, but at the boiling point of this solvent (101°) the metal ketyl would not go into solution, but merely formed a protective coating on the surface of the potassium, although the latter was molten.

Sugden [*Trans. Faraday Soc.*, **30**, 18 (1934)] has recently published some results for the magnetic susceptibilities of benzophenone potassium and *p*-biphenyl phenyl ketone potassium in dioxane which show that these metal ketyls are very highly dissociated in the solutions used. His results are in qualitative but not in quantitative agreement with ours. The difference may be due to the fact that the potassium rather than the sodium salt was used. We are not continuing the work because Sugden has promised to furnish more details soon.

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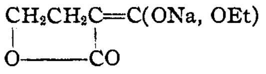
RECEIVED AUGUST 9, 1934

THE FORMATION OF ENOLATES FROM α-LACTONIC ESTERS

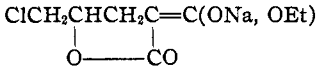
Sir:

Traube and Lehmann [*Ber.*, **34**, 1977 (1901)] treated an alcoholic solution of sodium enol malonic ester with ethylene oxide and obtained a sodium derivative of α-carbethoxybutyrolactone. In continuation of an investigation on the synthesis of lactones from malonic acid and related substances [Michael and Ross, THIS JOURNAL, **55**, 3684 (1933)] we deemed it important to prove experimentally its enolate structure, (I) [Meyer-Jacobson "Lehrb. org. Chem.," I^2, 641 (1913)]. We find that it can be reformed from the lactone and sodium ethoxide, that it reacts with methyl iodide to form the C-α-methyl derivative, and that treatment with iodine yields a mixture of two stereomeric dilactonic esters. These results definitely prove its enolate structure.



$$\begin{array}{l} CH_2CH_2C{=}C(ONa, OEt) \\ \,| \qquad\quad | \\ O\text{———}CO \end{array}$$

(I)



$$\begin{array}{l} ClCH_2CHCH_2C{=}C(ONa, OEt) \\ \qquad\ | \qquad\quad | \\ \qquad O\text{———}CO \end{array}$$

(II)

With epichlorohydrin, Traube and Lehmann [*loc. cit.*] isolated the enolate of α-carbethoxy-δ-chlorovalero-γ-lactone (II). On heating this compound with alcohol, and the formed viscous organic product with hydrochloric acid, Leuchs [*Ber.*, **40**, 307 (1901)] obtained a small yield of the γ,δ-dilactone (III). We find the first phase to be an intramolecular C-alkylation, leading to the cyclic tetramethylene lactonic ester (IV), which, on boiling with hydrochloric acid is converted into the γ-δ-dilactone.