$$2NaWO_3 \rightleftarrows 2Na + 2WO_3 \quad (1)$$

$$2Na + MoO_3 \longrightarrow Na_2O + MoO_2 \quad (2)$$

$$Na_2O + xWO_3 \longrightarrow Na_2WO_4(WO_3)_{x-1}\ x > 1 \quad (3)$$

The excess $(2 - x)$ of WO_3 dissolved in the unreacted bronze, forming bronzes with a deeper (red or blue) color showing a smaller lattice constant

$$NaWO_3 + yWO_3 \longrightarrow NaW^{V}O_3(W^{VI}O_3)_y,\ y = 2 - x \quad (4)$$

If the molybdenum(VI) oxide content was increased $Na_2W_2O_7$ as an added product, according to reaction (3), was formed.

Thus, as a final product, a mixture of a deeper colored bronze and molybdenum(IV) oxide resulted, while the sodium bitungstate was removed by the washing operation. Qualitative tests showed that there was only a trace of molybdenum in the sodium bronze. Therefore, molybdenum (VI) oxide was not dissolved by the bronze and acted only as an oxidizer, making solid solutions of the type $NaW^{V}O_3(Mo^{VI}O_3)_x$ impossible. Even the copper lid of the crucible (with larger amounts of molybdenum(VI) oxide present) was attacked: $Cu + MoO_3 \rightarrow MoO_2 + CuO$. This strong oxidizing property of molybdenum(VI) oxide at elevated temperatures was also observed by others.[7]

In the case of 30% molybdenum(VI) oxide, the reactions (2) and (4) proceeded far enough to leave very little of the original bronze which, in addition, was transferred into the tetragonal bronze because of the large amount of tungsten(VI) oxide dissolved according to (4). The formation of $Na_2Mo_2O_7$, and of a water-soluble compound $Na_2WO_4(MoO_3)_x$ $(x < 1)$ instead of (3) is also possible. The powder patterns of these three substances including $Na_2W_2O_7$ are identical except that the sodium tungstate containing molybdenum(VI) oxide has a contracted lattice.

The experiments performed with a sodium bronze containing 22% tungsten(VI) oxide at 1000° for two hours led to the same final products.

No molybdenum(VI) oxide containing sodium bronze was obtained when molybdenum was chosen instead of tungsten as a reducer

$$2Na_2WO_4 + 2WO_3 + Mo \longrightarrow 4NaWO_3 + MoO_2 \quad (5)$$

Of course, the bronze $NaWO_3$ always contained a dissolved excess of tungsten(VI) oxide.

All other combinations of the 3 substances, as shown on the left side of equation (5), being partly replaced by the corresponding molybdenum (or tungsten) compounds after the reaction at 800–900° in a vacuum gave only molybdenum(IV) oxide. The products such as Na_2WO_4, $Na_2W_2O_7$, Na_2WO_4 (MoO_3) and $Na_2Mo_2O_7$ were washed away in the subsequent treatment with water.

The Alkali Molybdenum Bronzes.—Completely replaced the initial products of reaction (5) by the corresponding molybdenum compounds, in no case gave any molybdenum bronzes. The chemical reason of the failure to prepare these bronzes might be as follows: For the formation of the bronzes it is necessary that the heavy metal should have the property to coexist in two valency stages at the elevated temperatures of formation. In the alkali tungsten bronzes tungsten is hexa- and pentavalent.[8] This, evidently, is impossible in the case of molybdenum bronzes because of the high oxidizing power of molybdenum(VI) oxide. Glemser and Lutz[9] showed that all lower molybdenum oxides above 700° were decomposed into molybdenum-(VI) and -(IV) oxides.[9] But four-valent molybdenum, similar to four-valent tungsten, does not enter the lattice of the bronzes.

The only possibility of obtaining molybdenum bronzes seemed to be by synthesis below 700°. Dry sodium molybdate, molybdenum(VI) oxide and molybdenum powder were heated in a vacuum in two separate experiments at 510 and 450° for 24 and 50 hours, respectively. After the soluble compounds were washed away, only molybdenum (IV) oxide remained.

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Adsorption and Reaction of Carbon Monoxide on Promoted Iron Catalysts

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Adsorption of carbon monoxide on iron catalysts has been the subject of many investigations,[1] and it has been inferred[1e,f,h] that it is possible to make such studies up to 150° without interfering chemical reactions. However, during the course of studies at 0–108° on the adsorption of carbon monoxide on potassium carbonate promoted iron catalysts, it has been found that chemical reactions occur that produce iron pentacarbonyl and carbon dioxide.

The experiments were carried out in an adsorption apparatus of conventional design[2] and operating at constant pressure.[3] The iron catalyst was of a type used for the synthesis of hydrocarbons from carbon monoxide and hydrogen. It consisted of mill scale in the form of a powder finer than 100 mesh, promoted with 0.5 wt. % K_2O.[4] After reduction with hydrogen at 340° under 250 p.s.i., the promoted catalyst was degassed at 450° until a pressure of 1.5×10^{-6} mm.

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[2] A. Weissberger, "Physical Methods of Organic Chemistry," Second Edition, Part I, Interscience Publishers, Inc., New York, N. Y., 1949, pp. 466–472.

[3] H. S. Taylor and C. D. Strother, THIS JOURNAL, **56**, 586 (1934).

[4] S. W. Walker, U. S. Patent 2,485,945 (October 25, 1949).

was obtained. Hydrogen adsorption experiments in this Laboratory indicated that temperatures from 350 to 400° remove most of the hydrogen, but it has been reported[5] that even under these conditions the surface will still contain some hydrogen. In each experiment the dead volume of the adsorption cell was determined with helium, and then the helium was pumped off at 350° until a vacuum of 10^{-6} mm. was obtained. The gas used in the adsorption experiments contained (in volume per cent.) 98.4 carbon monoxide, 0.1 carbon dioxide, 0.7 hydrogen and 0.8 nitrogen.

Four apparent adsorption isotherms were measured at 0, 25, 65 and 108° and 280 mm. pressure. The results, plotted in Fig. 1, cover only the first 11 hours of each experiment, although in each case the adsorption was followed much longer. Even after 144 hours, the catalyst was still "adsorbing" gas at a slow but finite rate. An experiment with an unpromoted mill-scale catalyst showed essentially the same "adsorption" isotherm at 25°.

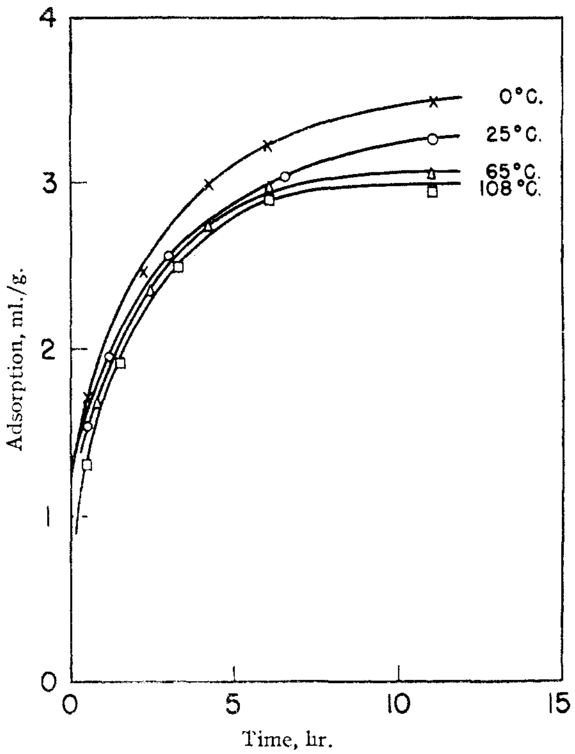

Fig. 1.—Apparent adsorption isotherms of carbon monoxide on a promoted iron catalyst.

After the measurement of each isotherm had been completed, a sample of the gas in the adsorption cell was transferred directly to the mass spectrometer for analysis. During this operation, the temperature and pressure of the cell were held constant to prevent readsorption. The gas analyses, given in Table I, unexpectedly revealed iron pentacarbonyl and large amounts of carbon dioxide. The absolute values of the iron pentacarbonyl concentrations are subject to some question, but comparisons of the concentrations at the different temperatures are believed to be valid.

TABLE I

COMPOSITION OF GAS IN ADSORPTION CELL AFTER 144 HOURS

Temp., °C.	Composition, volume per cent.				
	$Fe(CO)_5$	CO_2	H_2	N_2	CO
0	0.05	0.1	0.3	0.6	98.9
25	.6	8.9	.7	.8	89.0
25[a]	.6	9.1	.8	.9	88.6
65	.3	12.3	.3	1.0	86.1
65[a]	.3	12.0	.1	0.9	86.7
108	<0.05	16.7	.09	1.0	82.2

[a] Duplicate adsorption experiment.

The results indicate that, at temperatures as low as 25°, carbon monoxide will react with reduced iron to form iron pentacarbonyl. The concentrations of iron pentacarbonyl in the adsorption cell after 144 hours at 0 and 25° are lower than would have been predicted from equilibrium considerations[6]; it is assumed that this is the result of a low reaction velocity. The observed pentacarbonyl concentration at 65° is ten times the calculated value for some unexplained reason. At 108° the calculated concentration is 0.0038%, which is well below the sensitivity of the mass spectrometer.

The carbon dioxide in the adsorption cell could have been produced by the iron-catalyzed conversion of carbon monoxide to carbon and carbon dioxide. However, extrapolation of the kinetic data for this reaction[7] eliminates it as the source of the carbon dioxide. It is possible that the carbon dioxide, and presumably iron carbide, were produced by the decomposition of iron pentacarbonyl[8]; kinetic or equilibrium data on this reaction are not available.

In any event, the interpretation of carbon monoxide adsorption experiments at temperatures above 25° is subject to question unless gas analyses are made to confirm the absence of chemical reactions.

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Reversal of 2-Ethylhex-2-enal to Butyraldehyde

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Self-condensation of butyraldehyde leads *via* the aldol[1] to 2-ethylhex-2-enal[2] (I)

$$C_2H_5CH_2CHO \longrightarrow C_2H_5CH_2CHOHCH(C_2H_5)CHO \longrightarrow C_2H_5CH_2CH{=}C(C_2H_5)CHO \quad (I)$$

In an attempt to condense (I) with fluorene by azeotropic distillation in presence of freshly fused potassium hydroxide,[3] a hydrocarbon of m.p. 55°

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