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Schenectady, New York

REACTION RATE OF SOLID SODIUM WITH AIR

by

William H. Howland and Leo F. Epstein

October 19, 1953

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Introduction

The rate of reaction of sodium with air, and the effect of sodium purity and temperature on this process have recently been measured here.

It is generally known that chemical reaction rates are extremely sensitive to the purity of the reactants. For example, a freshly cut surface of triply distilled sodium will not oxidize nearly as rapidly as will commercial grade sodium. Distilled lithium (99.99% pure) can remain in air for ten (10) hours or longer before losing its metallic luster⁽¹⁾ but the surface of 99.9% pure lithium becomes completely blackened in a few seconds after exposure to air. It is reported⁽²⁾ that whereas 99.95% pure zinc dissolves completely in 10% HCl at room temperature, in the same time under identical conditions "chemically pure" zinc (99.99%) loses 53% by weight and "spectroscopically pure" zinc (99.999% or better) loses only 0.02%.

Other factors influencing the rate of the sodium-air reaction are the moisture content of the atmosphere and the temperature of the sample. In this experiment temperatures were maintained at 30°C, 55°C and 80°C $\pm$ 1°C while no attempt was made to control the humidity which averaged about 30% relative humidity at room temperature (25°C); consequently, the measured reaction rate is the sum of the rate of oxidation and the rate of formation of the hydroxide, each influencing the other, with the diffusion of air through the oxide-hydroxide layer as the rate determining factor. At low temperatures where the vapor pressure of water is low the hydroxide is moist

1. L. F. Epstein and W. H. Howland, *Science* 114 443 (Oct. 26, 1951).

2. Carpenter, H. and Robertson, J. M., *Metals*, Vol. I Oxford: Oxford Univ. Press 585 (1939).

and forms drops on the Na surface, eventually falling off. At higher temperatures, the oxide and hydroxide remain relatively dry. Unless controlled atmospheres are used to study these rates, it is possible to observe only the overall effect of the above conditions.

Experimental

Figure (1) shows one of the three thermostatted furnaces containing sodium filled pyrex "U" tubes of uniform cross section. Two "U" tubes were placed in each furnace - one containing triply-distilled sodium and the other containing filtered sodium. Commercial brick sodium was melted in a purified argon filled dry box and filtered through fritted glass filters into the "U" tubes. The composition of the filtered and distilled sodium is shown in Table I. The oxygen content in each case was assumed to be the equilibrium solubility at about 200°C.

The furnace consists of a 60 cm. length of 10 cm. diameter pyrex tubing open at both ends and heated on the inside by a lamp bulb type heating coil. Temperatures were controlled with Cenco bimetallic thermoregulators and measured with thermometers hanging vertically in the center near the exposed sodium surface. In order to avoid the danger of heating the sodium above its melting point (99.8°C), fuse wires of 50% by weight Bi-In alloy (M. P. 94°C) connected in series with the heating circuit were placed in the controlled temperature zone. Changes in the distance between a mark on the upper end of each sodium column and the Na - (Na_2O , NaOH) interface were measured with a ruler. As time progressed, the interface became extremely uneven on some of the samples and great difficulty was encountered in obtaining an average length of the column. Measurements were continued out to more than 1000 hours in each case.

TABLE I

<u>Filtered Na</u>		<u>Distilled Na</u>	
<u>Impurity</u>	<u>Percent</u>	<u>Impurity</u>	<u>Percent</u>
Fe	0.0008	Fe	0.0005
Ca	0.0500	Ca	0.0013
Cl	0.0015	Cl	0.0010
PO ₄	0.0003	PO ₄	0.0061
N	0.0010	Ni	0.0001
Heavy metals as Pb	0.0004	Co	0.0001
SO ₄	0.0010	Cr	0.00005
O	0.0050	O	0.0050
TOTAL 0.0600		TOTAL 0.0232	
% Na 99.940		% Na 99.977	

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Results

The experimental results were fitted to parabolic curves (characteristic of diffusion - limited processes) of the form $W(\text{g/cm}^2) = Kt^{1/2}$ by the method of least squares. The K values are given in Table II below. The probable error in W calculated from the constants is equal to or less than $\pm 0.1 \text{ g/cm}^2$. From figures 2, 3 and 4 it is apparent that at all three temperatures (30°C , 55°C and 80°C) filtered sodium has a higher rate of reaction than does the purer distilled sodium, and that the difference between the rates decreases with increasing temperature approaching the same value at the melting point (97.8°C). From the constants in Table I above, it appears that at the melting point the two rates would be the same to within the rather crude precision of these measurements. If this condition is included in a least-square fit to the rate data (fig. 5), the following relations are obtained:

$$\log K_D = -0.737 - 235 (1/T) \quad (\text{Distilled})$$

$$\log K_F = -1.88 + 190 (1/T) \quad (\text{Filtered})$$

and the respective activation energies are:

$$\Delta H_D = +1.07 \text{ K Cal/mole} - ^\circ\text{C} \quad (\text{Distilled})$$

$$\Delta H_F = -0.870 \text{ K Cal/mole} - ^\circ\text{C} \quad (\text{Filtered})$$

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TABLE II

	<u>FILTERED</u>	<u>DISTILLED</u>
T (°C)	$K(g/cm^2 - hr^{1/2})$	$K(g/cm^2 - hr^{1/2})$
30	0.057	0.031
55	0.049	0.039
80	0.044	0.038

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Fig 2

TEMPERATURE = 30°C

$W (g/cm^2)$

ENTERED

DISTILLED

$t^{1/2} (hr)^{1/2}$

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Fig 3

TEMPERATURE = 55°C

w (g/cm^2)

2.0

1.5

1.0

0.5

FILTERED

DISTILLED

$t^{1/2}$ (hrs $^{1/2}$)

40

30

20

10

11

Fig 4

w (g/cm²)

TEMPERATURE = 30°C

FILTERED
DISTILLED

$t^{1/2}$ (hrs^{1/2})

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t(°C)

97.8 80 55 30 5

log₁₀ K (g/cm²·hr)

61-6000

+ FILTERED } CALCULATED
 ⊙ DISTILLED }
 Δ OBSERVED

FILTERED

DISTILLED

3.0 1/T (°K)⁻¹ x 10³

2.5

3.5

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