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RESEARCH REPORT



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BA TTELLE FIELDS OF RESEARCH

AERO MAUTICAL ENGINEERING AGRIC ULTURAL CHEMICALS DEVELO PMENI ANALY TICAL CHEMISTRY APPLIE - MATHEMATICS BIOCH E MISTRY BIOPH YSICS BUILD : FIG AND ENGINEERING MATERIALS CATAL Y SIS AND SURFACE CHEMISTRY CERAMICS CHEMICAL ENGINEERING CHEMICAL PROCESSES CORROSION TECHNOLOGY COMPLITER ENGINEERING ECONOMICS ELECTRICAL ENGINEERING ELECTR CHEMICAL ENGINEERING ELECT R CHE MISTRY EXTRACTIVE METALLURGY ELECTRONICS FERROUS METALLURGY FOUND RY PRACTICE TECHNOLOGY FOOD FUELS AND COMBUSTION GRAPHIC ARTS TECHNOLOGY TECHNOLOGY GLASS HIGH - T EMPERATURE METALLURGY HUMA - ENGINEERING IMMUNICLOGY AND CANCER STUDIES INDUST RIAL PHYSICS INFORMATION PROCESSING INORGANIC CHEMISTRY

INSTRUMENTATION LIGHT ALLOYS AND RARE METALS LUBRICANT TECHNOLOGY MECHANICAL ENGINEERING METAL FINISHING METALLURGICAL PROCESSES MINERALOGY AND MICROSCOPY MINERALS PROCESSING MICROBIOLOGY NONFERROUS METALLURGY NUCLEONICS OPERATIONS RESEARCH ORGANIC CHEMISTRY ORGANIC COATINGS PETROCHEMICALS PETROLEUM ENGINEERING PHYSICAL CHEMISTRY PHARMACEUTICAL CHEMISTRY PRODUCTION ENGINEERING PULP AND PAPER TECHNOLOGY RADIOISOTOPES AND RADIATION RELIABILITY ENGINEERING REACTOR TECHNOLOGY REFRACTORIES RUBBER AND PLASTICS SEMICONDUCTORS AND SOLID-STATE DEVICES SYSTEMS ENGINEERING TEXTILES AND FIBERS THEORETICAL AND APPLIED MECHANICS THERMODYNAMICS WELDING AND METALS-JOINING TECHNOLOGY WOOD AND FOREST PRODUCTS

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TENTH QUARTERLY REPORT (Covering the Period: January 1 through March 31, 1963)

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ENGINEERING PROPERTIES OF POTASSIUM

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

by

Alexis W. Lemmon, Jr.

April 30, 1963

Contract NAS 5-584

Technical Management NASA-Lewis Research Center Space Electric Power Office

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TENTH QUARTERLY REPORT

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by

Alexis W. Lemmon, Jr.

INTRODUCTION

This program being performed at Battelle for the National Aeronautics and Space Administration (NASA) under Contract NAS 5-584 has as its objective the investigation of the engineering properties of potassium. This tenth quarterly report on this program covers work conducted from January 1 through March 31, 1963.

The thermodynamic and transport properties of potassium are being determined in the temperature range of 900 to 2100 F. Both liquid and vapor are of interest. Experimental values for vapor pressure, specific heat of liquid, thermal conductivity of liquid and vapor, viscosity of liquid and vapor, and P-V-T characteristics are being obtained. Experimental techniques for the direct measurement of the specific heat of potassium vapor have also been of interest. Subsequent to the measurements, the latent heat of vaporization, enthalpy, and entropy are to be computed from the measured data. It is anticipated that the information derived will be useful in the design, testing, and operation of nuclear electric-generating systems for use in space for which potassium is the working fluid.

SUMMARY

Measurements of the viscosity, vapor pressure, and heat content of liquid potassium have been concluded. In addition, thermal conductivity and electrical resistivity have been measured up to about 800 C; the apparatus has been modified and a small amount of potassium has been removed from the specimen container so that measurements up to 1150 C can be made as planned. Some minor question exists concerning the integrity of this Nb-1Zr alloy specimen container, however. Difficulties with migration of potassium into the balance chamber of the vapor viscometer have caused postponement of further attempts at measuring the vapor viscosity. Vapor compressibility measurements have been made in the P-V-T apparatus and results are reported; further analysis of these data and preparation of derived values for enthalpy, entropy, and specific heat are in progress. The design study of equipment for the direct determination of the specific heat of potassium vapor has been concluded. Further study of the dynamic bare-wire probe method for measuring the thermal conductivity of potassium vapor has been made; apparatus design is continuing. Topical reports covering the completed portions of this program are being prepared and distributed. The topical report covering the viscosity of liquid potassium (BATT-4673-T1) has been distributed. Final review of the topical report on the heat capacity of liquid potassium (BATT-4673-T2) has been accomplished and distribution should be made in a few weeks. Other topical reports are in preparation covering the experimental measurements of vapor pressure, the design study of equipment for the direct determination of the specific heat of potassium vapor, and the experimental measurement of vapor compressibility and computation of enthalpy, entropy, and vapor specific heat.

Measurements of the vapor pressure of potassium by means of a boiling point method have been concluded and experimental points and the derived equation have been plotted. Values for the heat of vaporization which have been derived from the vaporpressure data range from 910 Btu/lb at 1300 R to 609 Btu/lb at 2600 R.

The thermal conductivity and electrical resistivity of liquid potassium have been measured to about 800 C and tentative values have been reported previously. Modifications in the apparatus and in the amount of potassium in the specimen container have been made to permit measurements to 1150 C. Nondestructive testing of the specimen container is under way to investigate a suggested crack or porous region in a thin-walled section of the Nb-1Zr alloy material. Observed thermal conductivities of the Nb-1Zr container material, which range from 0.47 watt cm⁻¹C⁻¹ at 100 C to 0.66 watt cm⁻¹C⁻¹ at 1150 C, are also reported.

Additional modifications were made in the vapor viscometer which proved unsuccessful in preventing potassium condensate from entering the balance scale. Weightloss data taken before the scale was completely obscured were uncertain and no calculation of viscosity could be made. Plans relating to the future course of action for this item of the program are under consideration.

Determinations of the compressibility of potassium vapor in a constant-volume device have been concluded. Experimental compressibility data for potassium are tabulated and compared with values computed from the virial equation of state. Enthalpies, entropies, and vapor specific heats are being computed from the virial equation using known thermodynamic relationships.

Based on the best estimates of the properties of potassium vapor, a dynamic, bare-wire probe appears to be suitable for measuring the thermal conductivity of potassium vapor. Initial estimates indicate that corrections for the effects of convection and radiation should be possible. Work has started on the design of the physical apparatus, auxiliary equipment, and the electrical circuits.

EXPERIMENTAL MATERIALS

No additional special development work has been performed recently on either materials for construction or the purification of potassium. Procedures described in earlier quarterly reports are being followed for the Nb-1Zr alloy and the purification of potassium; these have been found suitable.

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DETAILS OF INDIVIDUAL PROGRAMS

Phase I - Item 1. Measurement of Vapor Pressure

(Joseph F. Walling and Harry K. Nuzum)

Measurements of the vapor pressure of potassium by means of a boiling point method have been concluded. Results are shown in Figure 1. The equation representing these data was given and discussed in the Eighth Quarterly Report⁽¹⁾.

The interest in values of vapor pressure is due in part to their use in calculation of the heat and entropy of vaporization. The heat of vaporization is related to the vapor pressure by means of the Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_{gas} - V_{liquid})} \quad . \tag{1}$$

When P represents the total pressure, the ΔH calculated refers to a reaction going from the liquid at its vapor pressure to the nonideal vapor at the vapor pressure.

By rearranging the Clapeyron equation the following can be obtained:

$$\Delta H_{vap} = T \left[V_{gas} \right] \frac{dP}{dT} - T \left[V_{liquid} \right] \frac{dP}{dT} .$$
 (2)

Differentiation of the vapor-pressure equation $(1)^*$ yields the following:

$$\frac{d(2.30259) \log P}{dT} = \frac{1}{P} \frac{dP}{dT} = \frac{11039.3}{T^2} \frac{-1.97108}{T} + 11.467 \times 10^{-4} - 4.9252 \times 10^{-7} T$$
$$+ \left(\frac{1.9136 \times 10^7}{T^3} - \frac{4410.4}{T^2}\right) e^{\frac{-4338.9}{T}} + \left(\frac{1.799 \times 10^9}{T^3} - \frac{1.704 \times 10^5}{T^2}\right) e^{\frac{-1.056 \times 10^4}{T}} .$$
(3)

By substituting Equation (3) into Equation (2) and using

$$PV_{gas} = RT + BP + CP^2$$
(4)

the following equation for calculation of ΔH_{vap} results:

$$\Delta H_{vap} = (RT^2 + BPT + CP^2T) \left(\frac{1}{P} \frac{dP}{dT}\right) - PT (V_{liquid}) \left(\frac{1}{P} \frac{dP}{dT}\right) \quad . \tag{5}$$

*References are listed on page 12.



FIGURE 1. VAPOR PRESSURE OF POTASSIUM BATTELLE MEMORIAL INSTITUTE

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This result permits calculation of $\triangle H_{vap}$ using only the vapor-pressure equation and values of liquid density. In order to do this cognizance must be taken of the fact that

BPT = -(2.3026) (82.057)T²
$$\left(\frac{1915.4}{T} e \frac{-4338.9}{T}\right) \frac{cm^3 - atm - degree}{mole}$$
 (6)

$$CP^{2}T = -2(2.3026) (82.057)T^{2} \left(\frac{7.40 \times 10^{4}}{T} e^{\frac{-1.056 \times 10^{4}}{T}}\right) \frac{cm^{3}-atm-degree}{mole} \quad . \quad (7)$$

The density of liquid potassium used in these calculations has been discussed previously.⁽²⁾

Results calculated in this manner are presented in Table 1. It should be emphasized that these numbers refer to the reaction

 K_{liquid} (Vapor Pressure) $\rightarrow K_{\text{nonideal gas}}$ (Vapor Pressure) . (8)

Uncertainties in values of ΔH_{vap} have been placed at ±100 cal/g-atom or ±5 Btu/lb.

TABLE 1.	HEAT OF VAPORIZATION OF
	POTASSIUM FROM THE
	LIQUID TO THE NONIDEAL
	VAPOR AT ITS SATURATION
	PRESSURE

т,	Т,	ΔH_{vap} ,	ΔH_{vap} ,
К	R	cal/g-atom	Btu/lb
722.4	1300	19770	910
777.9	1400	19550	900
833.5	1500	19310	888
889.0	1600	19030	875
944.6	1700	18720	861
1000.0	1800	18390	846
1055.7	1900	18010	828
1111.2	2000	17590	809
1166.8	2100	17110	787
1222.3	2200	16560	762
1277.9	2300	15930	733
1333.4	2400	15180	698
1389.0	2500	14290	658
1444.5	2600	13230	609

Phase I - Item 2. Measurement of Specific Heat of Liquid

(Edward A. Eldridge and Herbert W. Deem)

Results of this study have been reported in earlier quarterly reports and used in the preparation of a topical report, BATT-4673-T2, soon to be distributed.

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Phase I - Item 3. Measurement of Thermal Conductivity of Liquid

(Joseph Matolich, Jr., and Herbert W. Deem)

The thermal conductivity of liquid potassium has been measured to 800 C (1472 F) by a steady-state, longitudinal-heat-flow, comparative method. The method and apparatus have been described in previous reports.

Tentative thermal conductivities and tentative electrical resistivities were reported in the Eighth Quarterly Report. (1)

Thermal-conductivity measurements are to be extended to 1150 C (2100 F). Modifications of the apparatus to permit a higher sink temperature are completed. A small quantity of potassium has been removed from the specimen container to safely allow higher specimen temperatures without completely filling the sealed container.

During assembly of thermocouples on the specimen a faint line was observed on the container which suggested a crack or porous region. This region will be examined by nondestructive testing and a decision made on proceeding with the present container.

Some reduction of data has been made for the final report. Table 2 gives the experimental thermal conductivity of the Nb-1Zr container alloy at interpolated temperatures. Fifty-five observed points were reduced to fifteen by adjusting nearby points to a selected temperature and then averaging. The adjustment was along the slope of the curve. Because of the small temperature difference between the selected temperatures and the experimental temperatures, no adjustment exceeded 1.2 per cent.

Temperature, C	Thermal Conductivity, watt cm ⁻¹ C ⁻¹	Number of Points
100	0.472	3
175	0.490	8
250	0.508	7
325	0.517	4
400	0.529	4
475	0.552	3
550	0.55 ₂	6
625	0.559	3
700	0.57 ₈	4
775	0.575	5
850	0.598	2
925	0.62 ₀	1
1000	0.610	2
1075	0.610	1
1150	0.658	1

TABLE 2.	OBSERVED THERMAL CONDUCTIVITY OF Nb-1Zr
	CONTAINER MATERIAL, GROUPED DATA

During the next work period it is expected that the measurements will be completed.

Phase I - Item 4. Measurement of Viscosity of Vapor

(E. H. Hall and J. M. Blocher, Jr.)

A special capillary-flow-type vapor viscometer has been constructed for the measurement of the viscosity of potassium vapor in the range 900 to 2100 F. A description of the design and operation of the apparatus was given in the Fifth Quarterly Report.⁽²⁾

During the past quarter, modifications to the viscometer were made which were designed to prevent the potassium condensate from entering the balance chamber and obscuring the balance scale. The central duct was removed and in addition purified argon was admitted to the balance chamber and vented from the condensation chamber. Two additional potassium runs were then made. In the first run, a plug developed in the downstream vent line which interrupted the purge for a time. During this time, potassium entered the balance chamber and obscured the scale reading. The balance was cleaned and the run repeated after modifying the purge line to avoid the plugging. During this run, the argon purge was maintained continuously. Some improvement was noted. However, in spite of the purge, potassium was not completely excluded and after 20 minutes of operation the balance could no longer be read. The weight-loss data taken were uncertain because of the difficulty in reading the balance and no calculation of viscosity could be made.

Plans relating to the future course of action for this item are under consideration.

Phase I - Item 5. Measurement of Viscosity of Liquid

(E. H. Hall and J. M. Blocher, Jr.)

All results of this study have been reported in earlier quarterly reports and in topical report BATT-4673-T1(3).

Phase II - Item 1. Pressure-Volume-Temperature Measurements

(Joseph F. Walling)

Determinations of the compressibility of potassium vapor in a constant-volume device have been concluded.

Compressibility factors, PV/nRT, are the most general way of expressing the data taken. The results for the several virtual isotherms are presented in Table 3. The calculated compressibilities were determined from the following relations:

$$\frac{PV}{nRT} = 1 + B'P + C'P^2$$

$$\log |B| = 8.9912 + \frac{1.471 \times 10^3}{T} - 2.212 \log T$$
(9)

Pressure,	Volume,	Temperature,	Quantity,	Compressibility,	Compressibility,
atm	cm ³	K	g-atoms	PV/nRT	Calculated ^(a)
1 34	1074	1134. 0	0.01172	1, 320	0.940
1.54	1074	1134.5	0.01595	1, 192	0,923
1.05	1074	1133.0	0. 02204	0.974	0.909
1.07	1071	1133.6	0.01980	1.021	0,916
2 11	1074	1133.0	0.02752	0.885	0.894
1 97	1074	1133.	0.02594	0.877	0.903
2 26 (2 32)(b)	1014	1133	0.02374	0.017	0. /00
2. 20 (2. 52)		1155.3			
1.82	1076	1229.4	0.02136	0.909	0.949
3.60	1076	1229. ₁	0.0447 ₂	0.859	0.890
3.86	1076	1228.6	0.04724	0.872	0.880
3.37	1076	1229. ₂	0.04036	0.89 ₁	0.899
2.82	1076	1229 . 2	0.0328 ₄	0.916	0.917
2.27	1076	1229 . 2	0.02497	0.97 ₀	0.938
1.98	1076	1229 . 3	0.02219	0.95 ₂	0.947
2.52	1076	1229. <u>4</u>	0.02957	0.909	0.929
3.10	1076	1229.6	0.03638	0.909	0.909
4.59(4.61) ^(b)		1229.5			
1.74	1078	1287.9	0.01866	0.951	0.964
2,98	1078	1287.4	0.03482	0.873	0.931
4.25	1078	1286.9	0.0526_{0}	0.825	0.890
5.49	1078	1287.	0.06795	0.825	0.844
6.02	1078	1287.	0.0745_{3}	0.824	0.823
4.81	1078	1287. g	0.0576	0.85_{1}	0.871
3.59	1078	1287. 1	0.04176	0.87^{+}_{7}	0.912
2.32	1078	1287.	0.02517	0.941	0.949
6.42(6.63) ^(b)		1286.9			
6 84	1079	1324. 2	0.0875	0.77/	0.825
5 14	1079	1324.4	0.06002	0.850	0.883
3 74	1079	1325.1	0.0427 =	0.860	0.923
2 36	1079	1324 7	0 02251	1.040	0.957
1 64	1079	1324.	0.01636	0.99/	0.972
3 04	1079	1324.0	0.03662	0.824	0.941
4.42	1079	1324.	0.05232	0.830	0.904
5.84	1079	1323. 0	0.06937	0.834	0.860
1.63	1079	1321.4	0.01544	1,050	0.972
3. 04	1079	1322. 0	0.03502	0.863	0.940
4.47	1079	1321. 2	0.05220	0.852	0.901
5.90	1079	1320	0.07060	0.831	0.855
6 87	1079	1321 0	0.0874	0.782	0.822
7.50 (8.31) ^(b)	101/	1325. 1	0.00145	0.102	
1.04	1000	1280	0.0100	0 0 2 0	0.072
1.74	1080	1370.5	0.01984	0.939	0.714
4.02	1080	1369.9	0.04446	0.809	U. 732
0.10	1080	1369.7	0.0694 ₃	0.844	U. 881

TABLE 3. COMPRESSIBILITY DATA FOR POTASSIUM

Pressure, atm	Volume, cm ³	Temperature, K	Quantity, g-atoms	Compressibility, PV/nRT	Compressibility, Calculated(a)
8.14	1080	1370. 1	0.1041 ₀	0.751	0.821
7.13	1080	1369.5	0.08585	0.798	0.852
5.05	1080	1369.2	0.05248	0.925	0.908
2.99	1080	1369.6	0.03154	0.91_{1}	0.953
8.63	1080	1370. ₃	0.1117_9	0.74_{1}	0.805
1.60	1080	1371.0	0.01468	1.046	0.978
9.22(10.71) ^(b)		1370. ₅	Ū	Ū	
1.92	1082	1421.7	0.0182 ₈	0.974	0.978
5.40	1082	1422. 2	0.05739	0.873	0.921
8.81	1082	1423.3	0.1090 ₂	0.749	0.844
11.16	1082	1423.8	0.15527	0.666	0.778
9.53	1082	1423. ₂	0.12059	0.73 ₂	0.824
10.30	1082	1422.5	0.13535	0.70_{5}^{-}	0.802
7.50	1082	1422.0	0.08638	0.805	0.875
4.37	1082	1422.0	0.04564	0.888	0.940
6.49	1082	1421.6	0.07076	0.851	0.898
3.30	1082	1422.	0.03436	0.891	0.958
11.71 (14.17) ^(b)		1424.2	Ū	_	

TABLE 3. (Continued)

(a) From Equations (9), (10), and (11).

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(b) Apparent vapor pressures. Values in parentheses calculated from equation of Reference 1.

$$B' = -\frac{|B|}{82.057 \text{ T}}$$
(10)

$$\log |C'| = -6.315 + 4.670 \times 10^3 / T$$
(11)
C' < 0 .

Values for B and C were deduced from $spectral^{(4)}$ and $vapor-pressure measurements^{(1)}$, respectively. It is thought that compressibilities calculated using Equations (9), (10), and (11) are more reliable than direct experimental values. Further details and description will appear in the topical report.

Phase II - Item 2. Measurement of Specific Heat of Vapor

(Joseph F. Walling and Harry K. Nuzum)

A flow calorimeter for measuring the heat capacity of gases has been designed. Details will be forthcoming in a topical report.

Phase II - Item 3. Preparation of Enthalpy-Entropy Diagram

During the previous quarter Battelle's computer was programed to calculate the enthalpy and entropy of gaseous and gas-liquid systems. Since all necessary data became available during the quarter the calculations were carried out and an enthalpyentropy diagram is in preparation.

The enthalpy of potassium vapor at its vapor pressure, P_{vap} , for a selected temperature was calculated by adding the enthalpy of the liquid and the heat of vaporization. It remained then to calculate the quantity

$$\int_{\mathbf{P}_{vap}}^{\mathbf{P}} \left(\underbrace{\frac{\partial H}{\partial \mathbf{P}}}_{\mathbf{T}} d\mathbf{P} \right)$$
(12)

so that any arbitrary pressure could be selected. By using the virial equation of state and standard thermodynamics it may be shown that for any fixed temperature

$$H_{gas} - H_0^0 = H_1 - H_0^0 + \Delta H_{vap}$$

$$+ .0242179 \left[\left(B - T \frac{dB}{dT} \right) \left(P - P_{vap} \right) + \left(C - T \frac{dC}{dT} \right) \left(\frac{P^2 - P^2}{2} \right) \right] . \quad (13)$$

Values for the virial coefficients and their derivatives were determined by appropriate evaluation and differentiation of Equations (10) and (11).

$$H_1 - H_0^0 = -255.7 + 9.1506 T - 2.9943 \times 10^{-3} T^2 + 1.4865 \times 10^{-6} T (cal/g-atom)$$
. (14)

was obtained from liquid-enthalpy data⁽⁵⁾ by changing the reference state to 0 K,

$$\left[H_{273.2}^{o} - H_{0}^{o} = 1525 \text{ (cal/g-atom)}\right]^{(6)}$$

and temperature to Kelvin units. The calculation of the heat of vaporization has been described in this report.

In the manner exactly analogous to that used for the enthalpy calculation it may be shown that

$$S_{gas} = S_{liq} + \Delta S_{vap} - 1.98719 \ln P/P_{vap}$$

- .0242179
$$\left[\frac{dB}{dT} \left(P - P_{vap} \right) - \frac{dC}{dT} \left(\frac{P^2 - P^2}{vap} \right) \right] \qquad \text{where } P > 0 \quad . \tag{15}$$

The entropy of the liquid along the vapor-pressure curve S_{liq} was found by appropriate integration of the heat-capacity relation and the addition of 17.816 eu⁽⁶⁾ to yield third-law entropies.

The construction of an enthalpy-entropy diagram includes not only the gas phase but a two-phase region corresponding to varying proportions of the condensed and gas phases. Thus, for such a system

$$H_{syst} - H_0^o = x (H_1 - H_0^o) + (1 - x) (H_g - H_0^o) , \qquad (16)$$

where the following restrictions hold

 $1 \stackrel{>}{=} x > 0$ $P = P_{vap}$ for each temperature x = 0 $P_{vap} \ge P > 0$ for each temperature.

The diagram constructed from such calculations will be discussed and presented in a forthcoming topical report.

Phase III. Measurement of Thermal Conductivity of Vapor

The thermal conductivity of potassium vapor is to be measured over a temperature range from 900 to 2100 F.

Based on the best estimates of the properties of potassium vapor a dynamic-probe method appears to be suitable. A brief description of the probe and the mathematical region in which the response of the probe is expected to lie was given in the Ninth Quarterly Report. (5) The rate of effort on this phase has been reduced because of the demands of Phase I - Item 3. Because experimental work on Phase I - Item 3 has now been essentially concluded, the rate of effort on the vapor phase will increase.

Work has started on the design of the physical apparatus, auxiliary equipment and the electrical circuits.

An additional analysis is being made of the effects of convection and radiation in the probe apparatus on the results of the thermal conductivity measurement. Initial estimates indicate that both of these should be subject to correction.

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