The Vapor Pressure of Copper and Iron

BY A. L. MARSHALL, R. W. DORNTE AND F. J. NORTON

In the Langmuir method, vapor pressures are calculated from measured rates of evaporation by means of the equation[1]

$$m = \alpha \left(\frac{M}{2\pi RT}\right)^{1/2} P \qquad (1)$$

where m = rate of evaporation
α = accommodation coefficient
M = molecular weight
R = gas constant
T = absolute temperature
P = vapor pressure

In the case of graphite, the vapor pressures obtained in this way yield a heat of vaporization much higher than that calculated from spectroscopic data.[2] In view of this disagreement, it is desirable to test the validity of the Langmuir method by determining the rates of evaporation of elements at temperatures near which reliable equilibrium vapor pressure measurements are available. Harteck[3] has published the results of such measurements for copper. We have accordingly determined the rate of evaporation of this element at various temperatures to obtain the data necessary to test the Langmuir method in the case of copper. We have also determined the rates of evaporation of iron because such results have a bearing on the question of the magnitude of the accommodation coefficient α which is involved in the application of Equation (1). This equation becomes

$$\log P = \log m - \tfrac{1}{2} \log M + \tfrac{1}{2} \log T - 1.647 \qquad (2)$$

when P is expressed in atmospheres and m is in

grams per square centimeter per second. Equation (2) contains the additional assumption that the accommodation coefficient is unity.

The application of this method in general involves the assumption of unity for the accommodation coefficient. The validity of this assumption has been based upon the agreement obtained with equilibrium vapor pressure measurements. Nearly all direct experimental determinations of the accommodation coefficient differ from unity by amounts within the experimental errors, although this subject has not received extensive investigation. An accommodation coefficient of unity for liquid and solid mercury has been obtained by Knudsen[4] and by Volmer and Estermann.[5] Qualitative evidence in the present investigation indicates that the accommodation coefficients of copper and iron are also unity.

The effect of surface irregularities also must be considered in connection with the accommodation coefficient. The surface from which evaporation occurs may be appreciably greater than the surface calculated from the geometric dimensions of the specimen. The effect of surface crevices has been shown by Melville[6] to vary with the accommodation coefficient and to have no effect if the accommodation coefficient is unity. For solids with an accommodation coefficient of 0.9 the maximum error from this source would be 10% if all the cracks had angles less than 20°. It is probable that no significant error results from

(1) Langmuir, Phys. Rev., 2, 329 (1913).
(2) Marshall and Norton, THIS JOURNAL, 55, 431 (1933).
(3) Harteck, Z. physik. Chem., 134, 1 (1928).

(4) Knudsen, Ann. Physik, 29, 179 (1909).
(5) Volmer and Estermann, Z. Physik, 7, 1 (1921).
(6) Melville, Trans. Faraday Soc., 32, 1017 (1936).

taking the physical area of the specimen in this procedure. The consistency of the present results for solid and liquid copper amply justifies this conclusion.
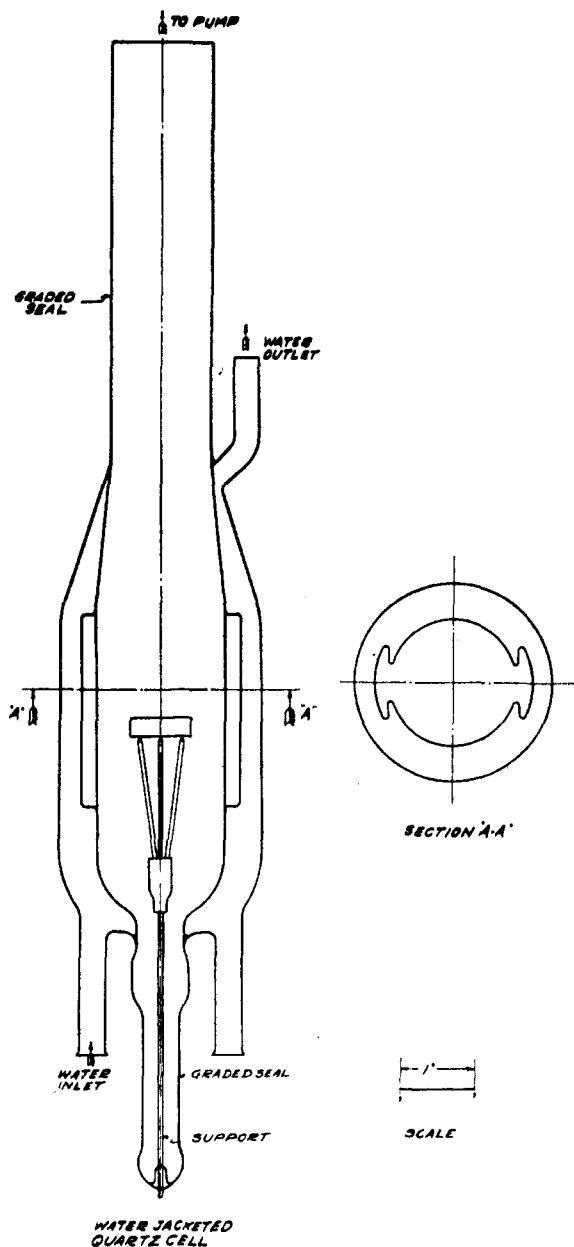

Fig. 1.—Quartz cell for high frequency heating in vacuum.

Experimental

The procedure consisted of the determination of the loss in weight by evaporation from metal rings of known surface area when the rings were heated by a high frequency induction furnace in a high vacuum at accurately determined temperatures for known time intervals. The metal specimens were rings 11 mm. i. d. and 22 mm. o. d. with thicknesses varying from 2.5 to

6 mm. The area from which evaporation took place varied from 7.65 to 11.70 sq. cm. The evaporation from the internal surface of the ring is subject to a small correction due to the fact that some of the evaporated atoms strike the surface and condense. This correction gives about a 2% reduction in the total area of the specimen. To determine the vapor pressure of liquid copper a slightly different specimen was necessary. For this purpose a molybdenum ring 22 mm. o. d. and 11 mm. i. d. and 5 mm. thick was turned with a 2 × 2 mm. groove in one face. A copper ring which fitted into this groove was fused in place in a hydrogen furnace after the molybdenum had been cleaned by electrolytic etching in sulfuric acid. The copper surface area on these specimens varied between 1.18 and 1.22 sq. cm. Molybdenum may be used for this purpose since it has no tendency to form an alloy with copper. The copper specimens contained the following impurities: As, Sb, Fe, Ni, Se and Te which together constituted only 0.015%. The iron specimens were made from electrolytic iron which had been hydrogen fired.

These metal rings were supported in a water-cooled quartz cell by three 60 mil pointed molybdenum prongs 5 cm. long which fitted in a molybdenum cylinder 6 mm. in diameter and 1.5 cm. long. This entire assembly was supported by a 60 mil tungsten wire which was attached to the cell through a graded seal. This construction and the quartz cell is illustrated in Fig. 1. The re-entrant angles in this cell (cf. Fig. 1, Section A-A) were designed to prevent the formation of a continuous metallic film on the quartz walls which would heat up in the high frequency field. No trouble was encountered from this source; the significance of this fact will be discussed later. The quartz cell was connected to the evacuating system by 3-cm. glass tubing. The entire apparatus was similar to that used in a previous investigation of gases in metals.

Hydrogen purified by diffusion through a palladium tube was pumped through the system during the bake-out to prevent the reaction of the desorbed water and oxygen with the metal specimen. The specimen was always thoroughly degassed after the bake-out. Preliminary experiments demonstrated that the measured losses in weight of the specimens were significant to 0.1 mg. The weight losses were also checked by analytical determinations of the evaporated metal. The technique of handling the specimens has been described previously.[7]

At the top of the containing vessel, 90 cm. from the metal specimen, there was an optical window through which temperature readings were taken with an optical pyrometer. A shutter operated through a water-cooled ground-glass joint protected the optical window from the metal vapor when the pyrometer was not in use. This precaution obviated many determinations of the absorption of the window.

Temperatures were measured with a disappearing filament type of optical pyrometer with a red filter (λ = 0.665 μ). The pyrometer field of view was about 3 mm. in diameter. A calibrated laboratory standard millivoltmeter in conjunction with a shunt was used to determine the filament current. The pyrometer readings

(7) Norton and Marshall, Trans. Am. Inst. Mining Met. Eng., 102, 287 (1932).

were taken under conditions which excluded all extraneous light from the observer's eyes. A series of pyrometer readings was taken at ten or twelve points uniformly distributed over the entire surface of the specimen; since these readings did not deviate by more than 5°, the error of the pyrometer, the individual values were averaged to give the temperature of the specimen. All pyrometer readings were checked by two observers.

The pyrometer was calibrated by comparison with a standard tungsten ribbon filament lamp which was supplied and calibrated by Dr. Forsythe[8] of the Nela Park Laboratory. Corrections for the absorption of the optical window were determined by calibrations with and without the window present. Since the absorption of the window was determined frequently the calibration of the pyrometer was checked frequently. During the experiments on copper the window correction was constant and equivalent to 2°. The window corrections during the iron experiments varied from 6 to 12°.

The pyrometer readings or brightness temperatures require a knowledge of the emissivities of iron and copper at λ = 0.665 μ in order to obtain true temperatures. The emissivity corrections for iron were determined directly by comparing pyrometer readings on the surface of the specimen with readings on the bottom of 1-mm. holes drilled to a depth of 3 mm. These holes served as black bodies and the corrections so determined agreed with the values given in the "International Critical Tables." The composite specimen of copper and molybdenum served to determine the emissivity corrections for copper since the emissivity corrections for molybdenum are available.[9] This composite specimen had an added advantage in the low temperature runs on copper because of the small emissivity correction for molybdenum compared to the correction for copper.

Results

The brightness temperatures and corresponding true temperatures for copper are given in Table I.

TABLE I

EMISSIVITY CORRECTIONS FOR COPPER

Brightness temp., °C.	True temp., °C.	Brightness temp., °C.	True temp., °C.
854	992 (S.)	930	1088 (S.)
866	1007 (S.)	953	1088 (l.)
858	990 (S.)	956	1096 (l.)
885	1027 (S.)	976	1115 (l.)
892	1039 (S.)	988	1134 (l.)
894	1042 (S.)	988	1143 (l.)
927	1081 (S.)	1021	1191
928	1084 (S.)	1025	1190

m. p.

These results are plotted in Fig. 2 and afford an independent check on the pyrometer calibration at the melting point of copper (1083°). The observed value for the melting point of copper was 1088°, indicating a 5° error in the temperature scale which is also the reproducibility of the pyrometer readings. No difficulty was encountered

(8) Forsythe, *J. Optical Soc. Am.*, **4**, 305 (1920).
(9) "International Critical Tables," Vol. V, p. 242.

in maintaining the solid–liquid equilibrium in the copper for several hours. This fact indicates the excellent temperature control which prevails in the induction furnace. The two phases were recognized easily due to the large difference in emissivities of solid and liquid copper.
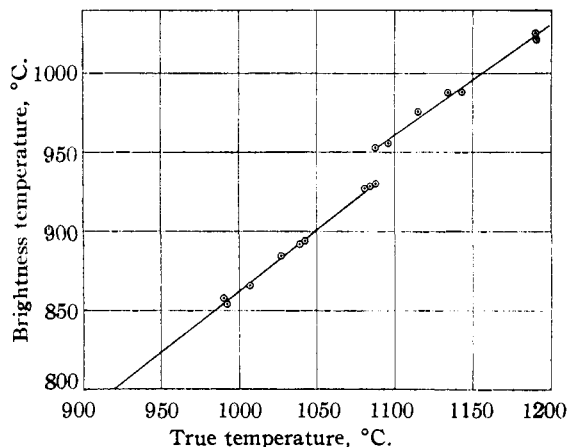

Fig. 2.

In the experimental procedure it is stated that the re-entrant portions of the quartz cell prevented the formation of a continuous metal film due to the condensation of the vapor on the surface. This fact constitutes a satisfactory demonstration of an accommodation coefficient of unity for iron and copper. In the re-entrant portions of the quartz cell sharp shadows were formed which would be impossible if the accommodation coefficient differed much from unity. This effect was demonstrated even more convincingly in the experiments with the copper embedded in molybdenum. In this case the copper deposit terminated in a sharp boundary where an extension of the upper plane of the specimen intersected the quartz cell wall.

It is desirable to compare the present vapor pressure measurements with each other and with previous results on a common basis; such a basis of comparison is afforded by calculating the heat of vaporization at 0°K. (ΔE_0°) for each determination. The free energy of an ideal gas is given by the equation

$$\left(\frac{F^\circ - E_0^\circ}{T}\right)_g = -\frac{3}{2} R \ln M - \frac{5}{2} R \ln T +$$
$$R \ln P - C - R \ln R - R \ln Q \quad (3)$$

where $Q = \Sigma p e^{-\epsilon/kt}$; p is the *a priori* probability and ϵ the energy of the state concerned. The other symbols in this equation have their usual significance.[10]

(10) Giauque, THIS JOURNAL, **52**, 4808 (1930).

<div align="center">TABLE II</div>

<div align="center">IRON VAPOR PRESSURE</div>

Run no.	T, °K.	Time, sec.	Loss, g.	$m \times 10^8$ g. cm.$^{-2}$ sec.$^{-1}$	P, atm.	Q	Σ	ΔE_0°, cal./g. atom
267	1317	80,100	0.0186	0.0303	3.32×10^{-9}	17.28	16.011	96,576
300	1341	37,800	.0177	.0612	6.78×10^{-9}	17.38	15.689	96,358
295	1381	21,600	.0306	.185	2.06×10^{-8}	17.52	15.164	95,912
261	1410	8,400	.0256	.398	4.52×10^{-8}	17.63	14.825	95,737
284	1437	7,200	.0323	.587	6.73×10^{-8}	17.73	14.650	96,418
286	1459	4,500	.0449	1.304	1.50×10^{-7}	17.80	14.290	95,489
270	1502	3,120	.0659	2.76	3.24×10^{-7}	17.94	13.941	95,902
270	1514	3,960	.0938	3.10	3.64×10^{-7}	17.99	13.883	96,266
270	1525	1,800	.0653	4.74	5.60×10^{-7}	18.02	13.692	95,632
286	1527	3,600	.1165	4.23	4.99×10^{-7}	18.03	13.741	96,100
286	1553	900	.0559	8.11	9.66×10^{-7}	18.12	13.443	95,617
259	1579	732	.0735	13.13	1.22×10^{-6}	18.19	13.328	96,386

Fe area = 7.65 sq. cm.   Mean ΔE_0° = 96,033 ± 310 cal./g. atom.

<div align="center">COPPER VAPOR PRESSURE</div>

Run no.	T, °K.	Time, sec.	Area, cm.^{2}	Loss, g.	$m \times 10^8$ g. cm.$^{-2}$ sec.$^{-1}$	P, atm.	Σ	ΔE_0°, cal./g. atom
8	1268	7,200	11.7	0.0437	0.52	5.24×10^{-8}	13.998	81,293
6	1269	10,800	11.7	.0446	.35	3.53×10^{-8}	14.169	82,350
21	1271	18,000	1.22	.0119	.54	5.44×10^{-8}	13.993	81,456
7	1301	3,900	11.7	.0553	1.21	1.24×10^{-7}	13.631	81,221
9	1309	2,400	11.7	.0518	1.84	1.73×10^{-7}	13.445	80,606
19	1315	7,200	1.18	.0154	1.81	1.78×10^{-7}	13.470	81,126
20	1318	7,205	1.17	.0159	1.88	1.93×10^{-7}	13.433	81,087
11	1320	7,860	1.22	.0210	2.19	2.25×10^{-7}	13.367	80,812
12	1356	5,700	1.22	.0497	6.89	7.18×10^{-7}	12.853	79,823
13	1356	5,045	1.22	.0443	7.20	7.50×10^{-7}	12.834	79,705
16	1436	558	1.22	.0210	30.8	3.30×10^{-6}	12.153	79,929
17	1438	600	1.22	.0214	30.2	3.24×10^{-6}	12.162	80,099
18	1466	398	1.18	.0262	55.8	6.11×10^{-6}	11.872	79,712

Mean ΔE_0° = 80,709 ± 600 cal./g. atom.

This equation upon introducing values of the constant terms reduces to the more convenient form

$$\left(\frac{F^\circ - E_0^\circ}{4.58\,T}\right)_g = -{}^3/_2 \log M - {}^5/_2 \log T +$$
$$\log P - \log Q + 1.586 \quad (4)$$

when P is expressed in atmospheres. For the condensed phase the values of $[(F^\circ - E_0^\circ)/4.58\,T]_s$ have been calculated from the thermodynamic properties of iron tabulated by Austin;[11] For copper the thermodynamical properties given by Kelley have been used.[12] The values of Σ and ΔE_0° have been calculated from the relations

$$\Sigma = +{}^3/_2 \log M + {}^5/_2 \log T - \log P + \log Q - 1.586 +$$
$$\left(\frac{F^\circ - E_0^\circ}{4.58\,T}\right)_c \quad (5)$$

$$\Sigma = \Delta E_0^\circ / 4.58\,T$$

The energy levels for the calculation of Q were obtained from the tabulation by Bacher and Goudsmit.[13] Only the first five states of iron need to be considered for our purpose; their a priori

(11) Austin, Ind. Eng. Chem., **24**, 1225 (1932); **24**, 1388 (1932).

(12) Kelley, Bureau of Mines Bull., 383 (1935).

(13) Bacher and Goudsmit, "Atomic Energy States," McGraw-Hill Book Co., Inc., N. Y., 1932.

probabilities are 9, 7, 5, 3 and 1, respectively, and their separations are: 0, 416, 704, 888 and 978 cm.$^{-1}$, respectively. For Fe(g) the contributions of higher energy states to the Q summation amount to only 0.05 at 1600°K. for the sixth to the tenth states inclusive. This contribution to Q would change our ΔE_0° values by 10 calories or less and therefore has been neglected. The Q values were calculated at 100° intervals for the temperature range involved, and interpolated for the experimental temperatures. For copper only the ground state contributes with an a priori probability of 2.

The experimental results on the vapor pressures of iron and copper are given in Table II which includes all of the completed runs. For each determination of a vapor pressure the heat of vaporization at 0°K. (ΔE_0°) has been calculated and affords a rigorous test of the consistency of the data.

Discussion

The experimental data in addition have been tested for consistency by plotting the quantity Σ

against $1/T$ as shown in Fig. 3 for iron and Fig. 4 for copper. The straight line in each plot is drawn so as to represent the mean values of ΔE_0°, which for iron is 96,033 ± 310 cal./gram atom and for copper the weighed mean or "best" value is 81,240 ± 740 cal./gram atom. These plots consequently give the deviation of each individual datum from the mean value. The numbers beside each experimental point in these plots give the value of ΔE_0° in kcal.
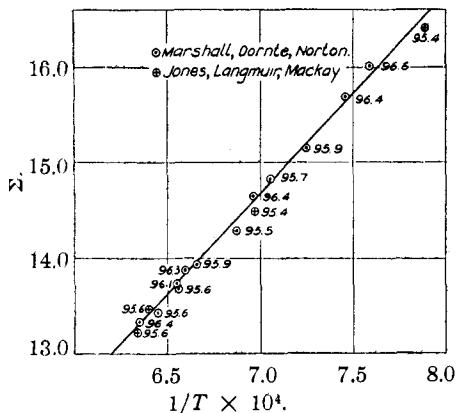

Fig. 3.

It is of interest to compare the present data with the previous determinations on the basis of the ΔE_0° values as shown in Table III for iron and copper. For iron the results of Jones, Langmuir and Mackay[14] have been used while the results of Greenwood[15] giving a boiling point of 2450°K. and of Ruff and Barman[16] giving a vapor pressure 36 mm. at the same temperature have been excluded because of the uncertainties in technique. The results of many determinations on copper have been used for similar calculations and also are tabulated in Table III.

TABLE III

T, °K.	P, atm.	ΔE_0°, cal./g. atom	Observers[17]
		Iron	
1270	1.40 × 10⁻⁹	95,427	J., L. and M.
1438	9.75 × 10⁻⁸	95,432	J., L. and M.
1562	1.01 × 10⁻⁶	95,598	J., L. and M.
1580	1.61 × 10⁻⁶	95,629	J., L. and M.
	Mean	95,522	

(14) Jones, Langmuir and Mackay, *Phys. Rev.*, **30**, 201 (1927).
(15) Greenwood, *Proc. Roy. Soc.* (London), **82**, 396 (1909).
(16) Ruff and Barman, *Z. anorg. Chem.*, **88**, 404 (1914).
(17) Harteck, *Z. physik. Chem.*, **134**, 1 (1928); Fischer and Grieger [cited by Sherman, *Chem. Rev.*, **11**, 93 (1932)]; Jones, Langmuir and Mackay, ref. 14; Greenwood, *Proc. Roy. Soc.* (London), **82**, 396 (1909); **83**, 483 (1910); Baur and Brummer, *Helv. Chim. Acta*, **17**, 958 (1934); Ruff and Bergdahl, *Z. anorg. Chem.*, **106**, 89 (1919); Ruff and Konschak, *Z. Elektrochem.*, **32**, 515 (1926); Ruff and Mugden, *Z. anorg. Chem.*, **117**, 147 (1921).

Copper

1420	1.40 × 10⁻⁶	81,503	H.
1447	1.80 × 10⁻⁶	82,244	H.
1463	2.90 × 10⁻⁶	81,706	H.
	Mean	81,807 ± 300	
2490	1.39 × 10⁻¹	81,529	F. and G.
1186	2.84 × 10⁻⁹	83,037	J., L. and M.
1298	4.34 × 10⁻⁸	83,733	J., L. and M.
2580	1.00	73,463	G.
2720	1.00	76,913	G.
1768	3.70 × 10⁻³	71,961	B. and B.
1834	6.90 × 10⁻³	72,153	B. and B.
1933	1.35 × 10⁻²	73,189	B. and B.
2023	2.70 × 10⁻²	73,538	B. and B.
2096	5.27 × 10⁻²	73,199	B. and B.
2116	6.50 × 10⁻²	72,974	B. and B.
2378	1.60 × 10⁻¹	76,902	R. and B.
2448	2.70 × 10⁻¹	76,218	R. and B.
2488	4.00 × 10⁻¹	75,640	R. and B.
2518	5.30 × 10⁻¹	75,054	R. and B.
2573	9.88 × 10⁻¹	73,323	R. and B.
2138	2.10 × 10⁻²	78,454	R. and K.
2328	1.39 × 10⁻¹	76,044	R. and K.
2348	1.36 × 10⁻¹	76,782	R. and K.
2643	1.01	75,074	R. and K.
2148	2.63 × 10⁻²	77,837	R. and M.
2301	8.59 × 10⁻²	77,459	R. and M.
2368	1.35 × 10⁻¹	77,415	R. and M.
2493	5.06 × 10⁻¹	74,615	R. and M.
2531	7.31 × 10⁻¹	73,771	R. and M.

The agreement in values of ΔE_0° for iron obtained in the present investigation, 96,033 ± 310, and earlier value obtained by Jones, Langmuir and Mackay, 95,522 ± 100, is satisfactory. This agreement is illustrated in Fig. 3 and is further
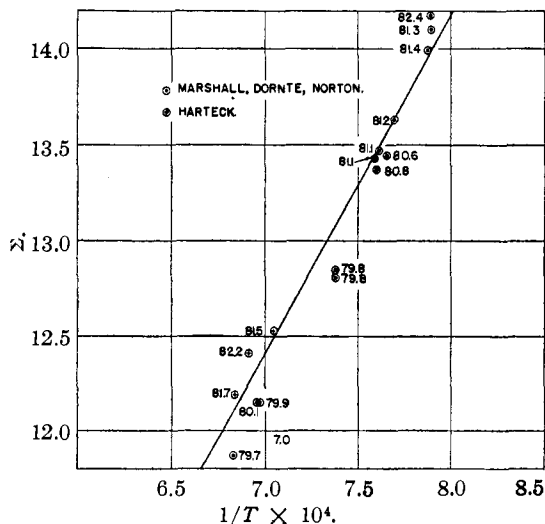

Fig. 4.

confirmed by a direct comparison of the measured rates of evaporation. It must be concluded from these comparisons of the two sets of data that the

deviations are within the error of the temperature determinations.

Harteck's results are included in Fig. 4 and are in satisfactory agreement with the present results. Harteck obtains an average value for ΔE_0° of 81,807 $\pm$ 300, which is a little higher than our value of 80,709 $\pm$ 600. This latter value is in agreement with the one value ($\Delta E_0^\circ = 81,529$) obtained by Fischer and Grieger. It should be pointed out that Harteck's results were obtained from the rate of effusion of saturated vapor through an aperture of known size so that the accommodation coefficient is not involved. The two values of ΔE_0° obtained by Jones, Langmuir and Mackay give an average of 82,966 cal. per gram atom, which is considerably higher than the values of three investigations which are in agreement. The other values of ΔE_0° in Table III are uniformly low and probably result from uncertainties in the emissivity corrections for copper.

It should be noted that a systematic trend occurs in the present values of ΔE_0° for copper. The values for solid copper lead to a mean ΔE_0° of 81,244 cal. per gram atom while the values at the

melting point and above give a mean ΔE_0° of 79,-853 cal. per gram atom. This trend indicates a systematic error in the results which we are unable to explain and makes impossible an accurate calculation of the small heat of fusion of copper. In the present case a value of 81,240 cal. per gram probably represents the "best" value for ΔE_0°, which is also the value Kelley[12] derives from Harteck's results.

Conclusion

The rates of evaporation of iron and copper have been used to determine the vapor pressures of iron and copper. The accommodation coefficient for these two metals appears to be unity, which apparently establishes the validity of the Langmuir method. Direct determinations of the emissivities of iron and copper have been made in conjunction with the vapor pressure study. The values of ΔE_0° for iron and copper are 96,033 and 81,240 cal. per gram atom, respectively. These values are shown to be in agreement with previous reliable determinations.

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The Mechanism of Cellulose Benzylation

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The more or less general acceptance of the primary valence chain theory of cellulose constitution has shifted interest to (1) the finer physical or morphological structure of cellulose fibers, and (2) problems of reaction kinetics. That both fields are inter-related is obvious. Any progress made in one will make possible important conclusions in the other. The importance of certain structural elements, such as growth rings, fibrils and especially the "skin system" (cuticle, primary cell wall, etc.), often has been emphasized,[1,2] while the function of the recently described ellipsoid particles[3] in the native fiber awaits interpretation. One of the most important questions related to the mechanism of cellulose reactions is the existence and size of submicroscopic structural units (micelles or crystallites). It has been

claimed that *all* cellulose reactions are of the so-called "micellar-heterogeneous" type.[4] However, there is evidence[5,6] to support the view that cellulose reactions do not follow a single pattern, and that the *type* varies, depending on the reaction partner, its concentration, the reaction medium, temperature, etc. It is quite probable that *all* the reaction models, worked out for microheterogeneous systems, such as surface reactions, topochemical macroheterogeneous reactions, permutoid or quasi-homogeneous reactions, as well as the previously mentioned micellar heterogeneous reactions, may apply to cellulose in one case or another, depending on circumstances.

These various reaction types are differentiated by the ratio of reaction velocity and internal dif-

(1) K. Hess and B. Rabinowitsch, *Kolloid Z.*, **64**, 257–268 (1933).

(2) K. Hess and L. Akim, *Cellulosechem.*, **12**, 95–103 (1931).

(3) W. K. Farr and S. H. Eckerson, *Contrib. Boyce Thompson Inst.*, **6**, 189–203, 309–313 (1934).

(4) K. Hess and C. Trogus, *Z. physik. Chem.*, **B15**, 157–222 (1932).

(5) A. L. Bernoulli, M. Schenk and F. Rohner, *Helv. Chim. Acta*, **17**, 897–918 (1934).

(6) D. Krüger, M. Lüdtke and F. Oberlies, *Angew. Chem.*, **47**, 806–10 (1934).