methyl peroxide,[1] $CH_2OHOOCH_2OH$. Investigation of the reaction at temperatures from 300 to 525° under widely different conditions has shown that the two principal primary reactions are the formation of ethylene oxide and of formaldehyde. The other reaction products, dioxymethyl peroxide, acetaldehyde, formic acid, the oxides of carbon, hydrogen and water are formed in a step-wise sequence[2] of follow reactions. At temperatures above 500° the thermal polymerization of ethylene becomes an important reaction even in the presence of appreciable amounts of oxygen and inert gases.[3]

The velocity of reaction is proportional to the cube of the ethylene concentration and is almost independent of oxygen, as has been shown by Thompson and Hinshelwood.[4] Comparison of the rates of reaction in packed and unpacked vessels shows that the reaction is mainly homogeneous. The reaction has an induction period which decreases with increase in temperature. It appears that the reaction follows a chain mechanism though it is necessary to assume that the chains can be both continued and stopped by the surface of the vessel.

Evidence of the formation of hydrogen peroxide as a reaction product has been obtained.

A full account of this work will appear shortly.

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INTERATOMIC FORCES IN BINARY LIQUID ALLOYS. QUANTITATIVE DETERMINATION FROM THERMODYNAMIC DATA

Sir:

It is generally agreed that the attractive force between non-polar molecules varies inversely as some high power (*e. g.*, the 9th) of the distance. Langmuir [This JOURNAL, **38,** 2246 (1916)] has emphasized that the forces holding together such molecules are acting almost wholly between molecules *in contact* and that, as a very good approximation, all forces acting at greater distances may be neglected. The quantitative treatment of the properties of liquids in terms of power laws of force involves great mathematical difficulties when one attempts to consider molecules of irregular shape. Langmuir has shown that the problem may be greatly simplified

[1] Legler, *Ann.*, **217**, 381 (1883); Nef, *ibid.*, **298**, 202 (1897); Baeyer and Villiger, *Ber.*, **33**, 2479 (1900); Fenton, *Proc. Roy. Soc.* (London), A90, 492 (1914); Rieche. "Alkylperoxide und Ozonide," Theodor Steinkopff Verlag, Dresden und Leipzig, Germany, 1931, p. 48.

[2] Bone and Wheeler, *J. Chem. Soc.*, **85**, 1637 (1904); Blair and Wheeler, *J. Soc. Chem. Ind.*, **42**, 415T (1923).

[3] Willstätter and Bommer, *Ann.*, **422**, 36 (1921).

[4] Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), A118, 170 (1928).

by regarding these van der Waals forces as coming into play between molecules only at the areas of contact. By using the concepts of surface area of individual molecules, and of interfacial energy for the contact surfaces, and assuming random orientation, he has developed through the Boltzmann equation ["Colloid Symposium Monograph," **3,** 48 (1925)] an expression for the deviation of activities from Raoult's law in binary liquid mixtures. So far as I know this relation has never been tested in binary liquid alloys where the situation is much simpler than in the cases of the organic mixtures discussed by Smyth and Engel [THIS JOURNAL, **51,** 2646 (1929)]. The equation is $\ln a_1/N_1 = \beta^2 S_1 \lambda/kT$ or $\ln a_2/N_2 = \alpha^2 S_2 \lambda/kT$, where $a = p/p°$, p being the partial vapor pressure, $p°$ the vapor pressure of the pure liquid, N the mole fraction, S the surface area per molecule, λ the energy per sq. cm. of interface between the two kinds of molecules, k the Boltzmann constant, T the absolute temperature and α and β are the surface fractions of the two components in the solution defined by $\alpha = N_1 S_1/(N_1 S_1 + N_2 S_2)$ and $\beta = N_2 S_2/(N_1 S_1 + N_2 S_2)$. The activity a may also be evaluated from electromotive forces of concentration cells. The ordinary molecular volume V which equals molecular weight/density, must be multiplied by 0.76 to take account of cubic or hexagonal close packing in the liquid, and divided by the Avogadro number to get the effective volume of a single molecule, $v = 4/3\pi r^3$. From this $S = 4\pi r^2$.

The thermodynamic data presented herewith are based upon electromotive force measurements of N. W. Taylor [This JOURNAL, **45,** 2884 (1923)] and of Hildebrand and Sharma [ibid., **51,** 467 (1929)]; density values from Hogness [ibid., **43,** 1621 (1921)] have been used.

INTERFACIAL ENERGIES BETWEEN METAL ATOMS IN LIQUID ALLOYS

System	Temp., t	Component 1	Component 2	Log a/N $N = 0$	$S \times 10^{16}$, sq. cm.	λ Ergs/sq. cm.
Zn–Cd	540°	Zn		0.490	25.8	48.8
Zn–Cd	540°		Cd	.615	32.8	48.2
Cd–Pb	544°	Cd		.480	32.8	37.7
Cd–Pb	544°		Pb	.582	40.6	37.0
Cd–Sn	544°	Cd		.246	32.8	19.4
Cd–Sn	544°		Sn	.270	37.3	18.7
Tl–Sn	352°	Tl		.444	37.6	23.4
Tl–Sn	352°		Sn	.44	36.7	23.9
Zn–Sn	539°	Zn		.240	25.8	23.9
Zn–Sn	539°		Sn	.60	37.3	41.3

The test of the Langmuir equation lies in a comparison of the two λ values calculated for each system from log a/N and S of each component independently. For all systems except zinc–tin the agreement is good to 3%. Since the log a_2/N_2 values for the second component of each system were evaluated by the Duhem relation they are themselves uncertain to 1 or 2%. They are somewhat smaller than the values given in my original

paper which were based upon an incorrect extrapolation. The system zinc–tin is certainly abnormal as I pointed out in my original paper in 1923. In this case influences are present which inhibit random orientation of the molecules.

The Hildebrand equation for "Regular Solutions" $RT \ln a_1/N_1 = bN_2^2$ or $RT \ln a_2/N_2 = bN_1^2$ can be strictly true only when the two components have the same surface area per molecule. S_{Ti} exceeds S_{Sn} by only 2%, and this is the reason for the result found by Hildebrand and Sharma that "so far as the variation with N is concerned, this system corresponds perfectly to the definition of a regular system given by the senior author" (THIS JOURNAL, **51**, 66 (1929)].

The evidence presented thus lends support to Langmuir's equation and to the assumptions upon which it is based.

More extensive data and a fuller treatment of this problem will be presented in a later publication.

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RADIOCHEMICAL EQUILIBRIUM IN AMMONIA SYNTHESIS

Sir:

The attempt to calculate chemical equilibrium or a steady state attained by alpha radiation from the known yield per ion pair of the two opposing non-thermal reactions was first made for the synthesis and decomposition of water [Lind, *Trans. Am. Electrochem. Soc.*, **34**, 214 (1918)]. The case for ammonia is much more suitable since the system remains entirely homogeneous. The decomposition of ammonia has been measured by Wourtzel [*Le Radium*, **11**, 342 (1919)]. The yield in synthesis was determined in a flow system by Lind and Bardwell [THIS JOURNAL, **50**, 745 (1928)] to lie in the range $+M_{NH_3}/N_{(N_2 + H_2)} = 0.2$–0.3. Choosing 0.2 as the most probable value of $+M/N$ and the round number 1.0 (from Wourtzel) for the decomposition $(-M/N)$, Lind and Bardwell calculated that the equilibrium (at 25°) would be $(1.0/1 + 0.2) = 83.3\%$ decomposition, corresponding to *9.09%* NH₃ by volume.

Later Ponsaert [*Bull. soc. chim. Belg.*, **38**, 110 (1929)] redetermined the yield for synthesis as *0.32* and taking 1.08 from Wourtzel for decomposition calculated equilibrium at 13.5% NH₃ by volume. The actual equilibrium has now been experimentally determined by D'Olieslager and Jungers [*Bull. soc. chim. Belg.*, **40**, 75 (1931)] as only *4.7%* NH₃ by volume.

In calculating the equilibrium from the yields at the beginning of the opposing reactions where back-reaction is negligible, it has been assumed that the mechanisms of the two reactions at equilibrium are independent of