the organic acid was precipitated. The product was practically pure, but was further purified by reprecipitating it from dilute sodium hydroxide. The yield was 93%, m. p. 234–236°.

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Correction. **Para-Nitrophenyl Carbamyl Chloride and Para-Nitrophenyl Isocyanate.**—In a recent paper it was stated that the product of the action of phosgene on p-nitraniline was p-nitrophenyl carbamyl chloride.[1] While this is the primary product of the reaction mixture, it has been found that after recrystallization from hot carbon tetrachloride as recommended in the procedure, the final purified product is then free from halogen and is p-nitrophenyl isocyanate, m. p. 57.° The analysis given is incorrect. Determination of the nitrogen by the micro Dumas method gave the following results.

Anal. Subs., 3.322 mg.: N_2 gas, 0.577 cc. at 31° and 744 mm. Calcd. for $C_7H_4O_3N_2$: N, 17.07. Calcd. for $C_7H_5O_3N_2Cl$: N, 13.97. Found: N, 17.09.

The purified product with m. p. 57° is therefore p-nitrophenyl isocyanate[2] and is the reagent from which the urethans were prepared. It is evident that the p-nitrophenyl carbamyl chloride lost hydrogen chloride during the recrystallization from boiling carbon tetrachloride.

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COMMUNICATIONS TO THE EDITOR

INTERATOMIC FORCES IN BINARY ALLOYS

Sir:

Under this title, N. W. Taylor has recently published [THIS JOURNAL, **53**, 2423 (1931)] a test of Langmuir's theory of non-electrolyte solutions which seems to me unfortunate in three respects. Following Hildebrand and Sharma [*ibid.*, **51**, 467 (1929)], he has confused Hildebrand's definition [*ibid.*, **51**, 66 (1929)] of a "regular solution," for which at constant composition $T \log a_1/N_1$ is independent of the temperature, with that of a "symmetrical system," for which at constant temperature $\log (a_1/N_1)/N_2^2$

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[1] Shriner and Cox, THIS JOURNAL, **53**, 1601 (1931).

[2] This has also been noted by van Hoogstraten, Doctor's Dissertation Rijks University, Leiden, June 30, 1931.

is independent of the composition. His method of comparison is to compare one quantity calculated by means of an extrapolation with another calculated by an integration from a few experimental points and involving the first extrapolation and also a second one. He considers that the agreement with Langmuir's equation supports Langmuir's assumptions, but he does not give a comparison with the equations of Heitler and of Van Laar.

The test can be made directly with the experimental data, and the accompanying table shows the comparison for cadmium–lead alloys [Taylor, *ibid.*, 45, 28 (1923)]. The results for the other alloys, which are essentially the same, are omitted for the sake of brevity. The solutions appear not to be "regular," but the values of $T \log a_1/N_1$ decrease with increasing temperature somewhat more than the irregularities of the individual measurements. They are constant enough to make the use of their average in the comparison which follows preferable to the use of the measurements at any one temperature, even though the temperatures are not the same for all the compositions.

I have discussed elsewhere [*Chemical Reviews*, 8, 321 (1931)] the various theories as to the relation of the change in free energy to the composition. Heitler's theory gives "symmetrical systems" or $T \log a_1/N_1 = \alpha N_2{}^2$ (1); Langmuir's theory gives $T \log a_1/N_1 = \beta S_1 [N_2 S_2/(N_1 S_1 + N_2 S_2)]^2$ (2); Van Laar's theory and the more general theory I proposed give $T \log a_1/N_1 = \gamma V_1 [N_2 V_2/(N_1 V_1 + N_2 V_2)]^2$ (3). The S's are the molecular (or molal) surfaces, and the V's the corresponding volumes, and α, β and γ are constants. The comparison of these three equations is given in the last three rows of the table, with constants calculated for the most dilute

CADMIUM–LEAD ALLOYS

N_1	0.786	0.696	0.584	0.509	0.401	0.293	0.269	0.155	0.123
$N_2{}^2$	.046	.092	.173	.241	.359	.500	.534	.714	.709
$\left(\dfrac{N_2 S_2}{N_1 S_1 + N_2 S_2}\right)^2$	.064	.123	.220	.296	.421	.562	.594	.759	.806
$\left(\dfrac{N_2 V_2}{N_1 V_1 + N_2 V_2}\right)^2$	.074	.141	.246	.325	.453	.591	.623	.779	.823

$T \log a_1/N_1$

427°		56		123			244		328
436°	31		92		172			298	
466°						222			
476°		58		122			245		325
484°	32		95		169				
544°		54		117		219	239		318
572°		54		115			237		317
Av.	31	55	93	119	170	220	241	298	322
Eq. 1	19	39	72	101	150	210	224	299	322
Eq. 2	26	49	88	118	168	225	238	304	322
Eq. 3	29	55	96	127	177	231	244	305	322

alloys. Although the physical theories are quite different, the resulting equations do not differ greatly for molecules so similar in size as these metals. The agreement of equation (1) with the experiments is distinctly poorer than that of the other two equations, but the difference between these two is too small to choose between them, and either one checks the measurements almost within the experimental error. The results with the other alloys are equally indecisive. In fact, I know of no measurements, in systems for which the agreement might be significant, which agree distinctly better with the equation of Langmuir than with that of Van Laar, or *vice versa*. The choice of theory must rest on a more fundamental analysis, a further contribution to which I hope to publish shortly.

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THE FORMATION OF HYDROGEN PEROXIDE FROM HYDROGEN AND OXYGEN

Sir:

I have recently reported [THIS JOURNAL, **52**, 5106–5110 (1930)] that hydrogen peroxide is formed, along with water, when hydrogen–oxygen mixtures at atmospheric pressure are passed through a Pyrex reaction tube at 500–550°. Thermodynamic data [Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 496] indicate that the peroxide cannot have been formed via water

$$H_2 + \tfrac{1}{2} O_2 \longrightarrow H_2O \qquad (1)$$
$$H_2O + \tfrac{1}{2} O_2 \longrightarrow H_2O_2 \qquad (2)$$

but must have been produced directly

$$H_2 + O_2 \longrightarrow H_2O_2 \qquad (3)$$

Since hydrogen peroxide dissociates to give water, the question arises as to whether all the water formed passes through the peroxide stage, or whether a part comes direct from the elements.

An attempt was made to answer this by determining the ratio of peroxide to water formed under conditions leading to successively lower total conversions. If hydrogen peroxide were the only primary product, one should obtain something approaching pure peroxide in the limit. As the experimental results were on the whole inconclusive, it seems unnecessary to report them in full. However, a representative set of data may be of interest.

The data of the table refer to experiments in which $19H_2:1O_2$ mixtures were passed through a spherical Pyrex reaction vessel of 4.3 cm. diameter. The gases passed from flowmeters to traps cooled to $-79°$, then through