Summary

1. Large amounts of oxygen have been found to be instantaneously and irreversibly adsorbed by catalytically active nickel even at −190°. The amount of such low temperature sorption is greater the more active the surface. In general the amount of irreversible adsorption increases with the temperature.

2. Large amounts of reversibly adsorbed oxygen occur only at −190°.

3. Sintered and regenerated nickel surfaces possess certain like and different sorptive characteristics.

4. The rates of slow sorption are small at −190°, but increase with the temperature, and at a given temperature are greater the more active the surface.

5. The interpretation of the various phenomena observed makes it most probable that activated adsorption occurs even at −190° and is the major fraction of the oxygen sorbed at 0°.

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The Ternary System Diphenyl–Diphenylamine–Benzophenone

BY H. HOWARD LEE AND J. C. WARNER

Diagrams for the binary systems of diphenyl, diphenylamine and benzophenone were reported in a previous paper.[1] In the present investigation the freezing point–composition diagram for the *ternary* system of these components has been determined. The method of purification and the experimental procedure have been the same as in the previous investigation.

With most samples the initial crystallization temperature was checked by determining the temperature at which the solid phase disappeared. To accomplish this, a large number of solidified samples were placed in a thermostat set at a suitable temperature. After a period of from eight to ten hours, a record was made of samples which were completely liquid at the thermostat temperature. The temperature of the thermostat was then increased by from 0.1 to 1.0° depending upon the appearance of the remaining samples. After eight to ten hours, another record was made. The samples were freshly solidified each time the temperature of the thermostat was changed. This procedure for determining the temperature at which the solid phase disappeared was referred to as "thermostating" in a previous paper.[1]

Experimental Results.—The distribution of the samples used is indicated by the circles in Fig. 1. The experimentally determined initial

(1) Lee and Warner, THIS JOURNAL, **55**, 209 (1933).

crystallization temperatures, final solidification temperatures and temperatures for disappearance of solid are listed in Table I. The conventional ternary model, Fig. 2, was constructed from the data in Table I by inserting small steel rods of proper lengths to indicate temperatures in holes in a triangular wooden base representing compositions. The tops of the rods were pointed and the model was filled in with plaster of Paris to the tips of the rods. The intersections of the surfaces of the solid model are indicated by the boundary lines in Fig. 1. The intersections of these lines indicated approximately the eutectic compositions. A number of additional samples (not shown in Fig. 1) were then made up to determine more definitely the two ternary eutectic compositions and temperatures.

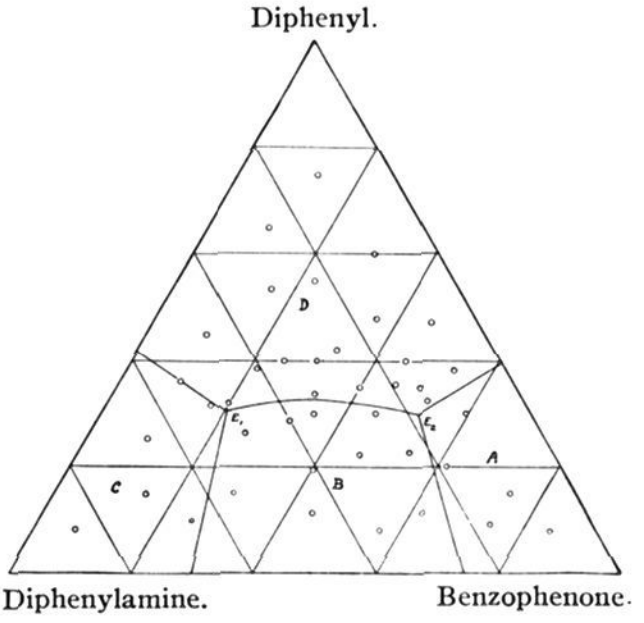

Fig. 1.

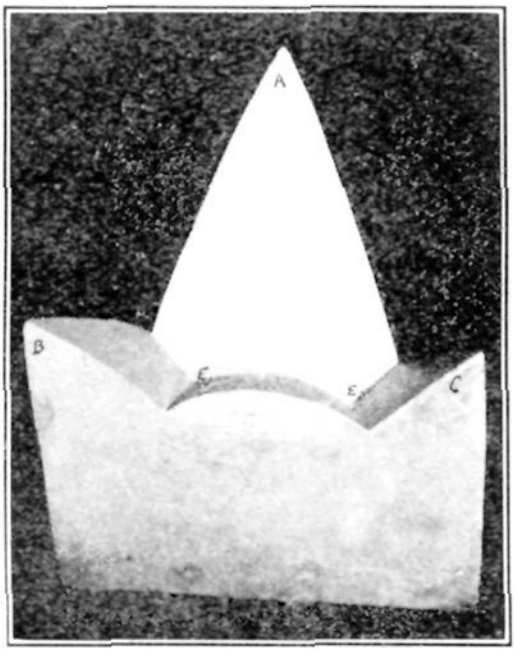

Fig. 2.—A, Diphenyl, m. p. 69.0°; B, diphenylamine, m. p. 52.8°; C, benzophenone, m. p. 47.7°; E_1 and E_2 are the ternary eutectics.

The ternary eutectic compositions (E_1 and E_2) are given in Table I. The average of seven final solidification temperatures yields a temperature of 18.8° for E_1. An average of eight final solidification temperatures gives 16.5° for E_2. From the solid figure and the data in Table I, the contours for the liquidus surfaces were plotted in Fig. 3.

In the investigation of the system diphenylamine–benzophenone,[1] it was found that the compound between the components existed in two forms; a stable form with a melting point of 40.2° and a metastable form melting at 30.8°. The existence of the metastable compound would lead one to predict two metastable ternary eutectics. We have been able to verify this prediction experimentally and have determined approximately the metastable eutectic compositions and tem-

peratures from cooling curves on freshly prepared samples, crystallized without inoculation, and the projection of the surfaces of the solid figure. Metastable E_1' has the approximate composition 28 mole per cent. diphenyl, 47 mole per cent. diphenylamine and 25 mole per cent. benzophenone. The approximate eutectic temperature for E_1', as determined from the average final solidification temperatures of seven samples, is 15.0°. The composition of E_2' is approximately 28.5 mole per cent. diphenyl, 20.5 mole per cent. diphenylamine and 51.0 mole per cent. benzophenone. From the average final solidification temperatures of four samples, the eutectic temperature for E_2' is 13.1°.

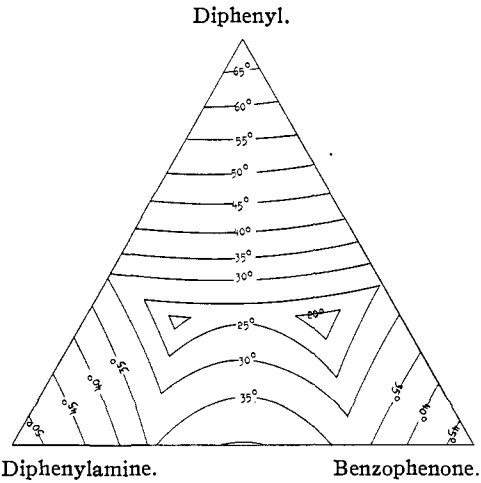

Fig. 3.

TABLE I

Region Fig. 1	Mole % $(C_6H_5)_2$	Mole % $(C_6H_5)_2NH$	Mole % $(C_6H_5)_2CO$	Init. cryst., °C.	Final solidification, °C.	Disapp. of solid, °C.
	8.0	7.0	85.0			40.3
	9.2	16.2	74.6	31.2		31.6
A	15.0	10.0	75.0	34.1		34.3
	20.0	18.0	62.0			24.3
	30.0	10.0	60.0	23.8		24.1
	8.0	35.0	57.0	34.3		34.9
	11.5	26.1	62.4	30.0		30.3
	11.2	44.4	44.4	34.4		35.2
	15.0	55.4	29.6	30.2		30.8
	19.7	40.15	40.15			31.8
B	22.2	31.0	46.8	28.0		29.0
	22.5	22.9	54.6			25.0
	26.1	48.2	25.7			24.9
	28.6	39.9	31.5	22.6	18.7	24.1
	30.0	35.0	35.0	25.5		25.7
	30.0	25.0	45.0	21.3	16.5	23.3
E_2	30.0	18.0	52.0	16.6	16.5	16.7
	8.0	85.0	7.0			45.4
	10.0	65.0	25.0	31.2		31.5
	15.0	70.0	15.0	35.8		36.0
C	25.0	65.0	10.0	32.8		33.4
	31.5	51.3	17.2	22.0	19.0	22.0
	36.0	54.0	10.0			25.7
E_1	30.5	49.0	20.5	18.8	18.8	19.0

TABLE I (*Concluded*)

Region Fig. 1	Mole % $(C_6H_5)_2$	Mole % $(C_6H_5)_2NH$	Mole % $(C_6H_5)_2CO$	Init. cryst., °C.	Final solidification, °C.	Disapp. of solid, °C.
	31.3	49.5	19.2	19.2	18.8	20.0
	31.1	48.8	20.1	19.0	18.7	19.6
	33.8	33.1	33.1			24.8
	35.0	25.0	40.0	23.3		23.9
	32.25	15.15	52.6	18.8	16.6	19.3
	30.9	16.7	52.4	17.2	16.5	17.8
	30.9	17.2	51.9	16.8	16.5	17.6
	35.0	15.0	50.0		16.6	22.7
	35.8	18.95	45.25			24.2
	38.0	8.0	54.0	24.6	16.5	25.1
	38.3	40.1	21.5	22.7	19.0	23.8
D	40.0	35.0	25.0	28.9	18.7	29.4
	40.0	30.0	30.0			29.4
	40.0	15.0	45.0	28.1	16.5	28.3
	42.0	25.0	33.0	30.5		30.7
	45.0	45.0	10.0	33.3		33.7
	47.0	7.0	46.0	34.0		34.2
	48.6	15.2	36.2	36.2		36.5
	53.8	30.1	16.1	40.9		41.4
	55.0	22.5	22.5			42.0
	60.0	10.0	30.0	43.8		44.2
	65.0	25.0	10.0	48.9		
	75.0	12.0	13.0	55.1		

Summary

The freezing point–composition diagram for the ternary system diphenyl–diphenylamine–benzophenone shows two stable ternary eutectics. One eutectic (E_1) has the composition 30.5 mole per cent. diphenyl and 49.0 mole per cent. diphenylamine. This eutectic temperature is 18.8°. The other eutectic (E_2) occurs at 30.0 mole per cent. diphenyl and 52.0 mole per cent. benzophenone, and at 16.5°.

Evidence is presented for the existence of two metastable ternary eutectics.

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