TABLE I

σ-CONSTANTS FOR THE CARBETHOXYL AND HYDROXYL GROUPS

Reaction	Solvent	Temp., °C.	log $k^{\circ a}$	ρ^a	σ (m-$CO_2C_2H_5$)	σ (p-$CO_2C_2H_5$)	σ (m-OH)
Ionization of benzoic acids	H_2O	20	-4.234^b	$+1.107^b$	.....	.....	$+0.040^b$
		25	-4.203^a	$+1.000^a$	.....	.....	$+ .124^c$
	50% EtOH	25	-5.71^d	$+1.464^d$	+0.348	+0.437	+ .068
Benzoic acids with diphenyldiazomethane	100% EtOH	30	-0.014^d	$+0.937^d$	+ .313	+ .336	− .123
Alkaline hydrolysis of ethyl benzoates	87.83% EtOH	30	-3.072^a	$+2.498^a$	.....	$+ .443^c$	.....
	56% acetone	25	-2.513^a	$+2.373^a$	$+ .243^{e,f,g}$	$+ .392^{e,f}$	.....
Phenols with acetyl bromide	Ethyl acetate	0	$-1.170^{h,i}$	-1.898^h	$+ .341^i$	.....	.....
Methyl benzoates with aniline	Nitrobenzene	100	-0.898^j	$+0.379^h$	.....	.....	$+ .040^j$
				Mean	+ .334	+ .402	+ .014

[a] Ref. 3. [b] Calculated from data of B. Jones and J. C. Speakman, *J. Chem. Soc.*, 19 (1944). [c] Calculated from the data of J. Shorter and F. J. Stubbs, *ibid.*, 1180 (1949). [d] Ref. 4. [e] Calculated after correcting the observed rate by a statistical factor of two. [f] Calculated from the data of E. Kivinen and E. Tommila, *Suomen Kemistilehti.*, **14B**, 7 (1941). [g] Not used in calculation of the mean. [h] Calculated from the data of H. L. Bassett, *J. Chem. Soc.*, 1313 (1930); 2516 (1931); H. L. Bassett and A. O'Leary, *ibid.*, 2945 (1932). [i] Relative value. [j] Calculated from the data of N. J. Vartak, N. L. Phalnikas and B. V. Bhide, *J. Indian Chem. Soc.*, 24, 131A (1947).

reactions and procedures have been described previously in detail.[4,5]

The apparent ionization constants in 50% aqueous ethanol (by volume) at 25.0 ± 0.1° were 6.31×10^{-6}, 8.42×10^{-6} and 2.45×10^{-6} for *m*-carbethoxy, *p*-carbethoxy and *m*-hydroxybenzoic acids, respectively. The second-order rate constants with diphenyldiazomethane at 30.0 ± 0.1° in 100% ethanol were 2.16, 2.27 and 0.843, respectively, (all in l. mole^{-1} min.$^{-1}$) for the same series of substituted benzoic acids. The alkaline saponification rate of diethyl terephthalate in 87.83% ethanol at 30.0 ± 0.1° was 1.28 l. mole^{-1} min.$^{-1}$. The σ-constants from the available data are summarized in Table I.

The mean σ-values obtained from the data of Table I are: *m*-carbethoxyl, +0.334, *r* (the median deviation) equal to 0.014; *p*-carbethoxyl, +0.402, *r* equal to 0.038; and *m*-hydroxyl, +0.014, *r* equal to 0.076. A σ-value of −0.34 has been obtained previously[4] for the *p*-hydroxyl group.

(4) J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, **71**, 2923 (1949).

(5) K. Kindler, *Ann.*, **450**, 1 (1926).

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The Solubility of Indium in Mercury

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In spite of the recent interest in alloys that are liquid at room temperature, the system mercury–indium has received little attention. Richards and Wilson[1] dissolved indium in mercury to the extent of 1.92% and found that the resulting amalgams are liquid at both 30 and 0°. Hildebrand[2] made amalgams containing up to 2.1% indium at 30°. Williams[3] in a study of the conductivity of liquid amalgams made an amalgam containing 3% indium. More dilute indium amalgams were used by Davies and Keeping.[4] None of these investigators attempted to determine the limit of the solubility of indium in mercury. Parks and Moran[5] investigated the solubility of indium in mercury over the temperature range 0–50°. They reported an increase in solubility from 1.23 weight % at 0° to 1.31 weight % at 50°.

It was in view of the paucity of the above data and their disagreement that this investigation was undertaken.

Preliminary tests indicated indium to be much more soluble than reported by Parks and Moran. It was therefore decided to investigate the entire range of compositions by means of cooling curves.

Experimental

The mercury used in this investigation was purified in the following manner. Air was bubbled through it for several hours to oxidize metallic impurities. It was filtered to remove the coarser particles of oxide and dirt, sprayed through a column of 3 N HNO_3, washed with distilled water to remove the acid and dried with filter paper. It was then vacuum distilled.

The indium used had a guaranteed purity of better than 99.97%. This high purity was confirmed by qualitative spectrographic analysis which showed only small amounts of cadmium and zinc. Its melting point was determined as 156.2°. There is considerable disagreement in the literature concerning the melting point of indium. Roth and Meyer[6] give 156.4°, Grube and Wolf[7] give 155°, while Denny, Hamilton and Lewis[8] give 156.1°.

An electric furnace for melting the alloys was constructed by modifying a tube furnace as follows. The furnace, which was approximately 15 inches in length with an opening approximately $^3/_4$ inch in diameter, was closed at one end with a plug of magnesia and arranged vertically. The outside wall of the furnace was wrapped with nichrome wire and covered with asbestos. This heating unit was left on while the sample was cooling to retard its rate of cooling. In this way rates of cooling ranging from 0.5 to 2.0° per minute were obtained.

This furnace was used in analyzing melts in the range beginning with those melting near pure indium down to about 60°. From this point, the furnace was replaced by a large tube with an air space to provide slower cooling. This outer tube was surrounded first by ice-water, then with

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(1) Theodore W. Richards and J. H. Wilson, *Z. physik. Chem.*, **72**, 129 (1910).

(2) Joel H. Hildebrand, THIS JOURNAL, **35**, 501 (1913).

(3) E. J. Williams, *Phil. Mag.*, **50**, 589 (1925).

(4) W. G. Davies and E. S. Keeping, *ibid.*, **7**, 145 (1929).

(5) W. G. Parks and W. G. Moran, *J. Phys. Chem.*, **41**, 343 (1937).

(6) W. M. Roth and I. Meyer, *Z. anorg. allgem. Chem.*, **214**, 315 (1933).

(7) G. Grube and W. Wolf, *Z. Elektrochem.*, **41**, 679 (1935).

(8) J. P. Denny, J. H. Hamilton and J. R. Lewis, *J. Metals*, **4**, 39 (1952).

calcium chloride solution–ice, and finally a Dry Ice–acetone-bath.

Temperature measurements were made with a copper-constantan thermocouple by means of a Leeds and Northrup precision type potentiometer No. 7551. This instrument could be read to one microvolt corresponding to a temperature difference of approximately 0.02°.

The thermocouple was made from No. 32 B and S gage copper and constantan wires. To prevent contamination of the melt and also to provide good thermal contact, the junctions were enclosed in fine glass tubes about 5 mm. long which were collapsed tightly upon the metal.

The thermocouple was calibrated against the following accurately known transition points: melting point of tin (231.85°), boiling point of water, transition temperature of Glauber's salt (32.384°), and melting point of mercury (−38.89°).

Studies were made first on the indium-rich alloys. These were prepared by adding the desired increments of mercury to the previously analyzed alloys in a 15 × 120 mm. test-tube. In a similar manner mercury-rich alloys were prepared. The volume of sample analyzed was limited to about 5 ml. The alloys were covered with mineral oil to protect them from oxidation and wetting the walls of the tube. All samples were cooled from above the melting point of indium to at least −10°.

Results.—The results are given in Table I and are plotted in Fig. 1.

TABLE I

Sample	Weight % indium	Liquidus temp., °C.	Solidus temp., °C.
1	100.00	156.2	156.2
2	97.46	151.3	148.9
3	90.12	135.1	125.8
4	84.07	121.7	90.2
5	79.30	108.2	...
6	74.70	94.2	...
7	69.84	78.1	...
8	64.89	59.2	...
9	60.01	37.6	...
10	54.92	10.3	...
11	49.98	...	...
12	45.01	...	...
13	40.04	...	...
14	32.98	...	...
15	25.01	...	...
16	20.00	...	...
17	14.95	...	...
18	10.06	...	...
19	4.93	...	...
20	0.00	...	...

Between 10° and the melting point of indium, 156.2°, the solubility of indium in mercury is expressed by the equation

$$\log N_2 = (122.13/T) + 0.0027625T - 1.4740$$

where N_2 is the weight fraction indium and T is in °K.

Since these results differ seriously from those reported by Parks and Moran[5] the following supplementary experiment was performed. At room temperature (approximately 25°), weighed portions of indium and mercury were mixed to yield two mixtures, containing 84.4 and 63.2% mercury. In each case, within a few minutes the indium seemed to have dissolved to yield a homogeneous liquid. To ensure that a two-phase system was not formed each mixture was subjected to centrifugation and then separate portions of the alloy were analyzed as follows: A sample was removed from the top of each mixture and another from the bottom. Each was weighed and treated with hot concentrated hydrochloric acid to dissolve the indium. The mercury, which was unattacked by the acid, was dried and weighed. The composition of the upper and lower samples were found to be essentially the same and equal to that of the total mixture. (In the case of the mixture containing 63.2% Hg, the lower sample analyzed 62.9% and the upper 63.0%.)

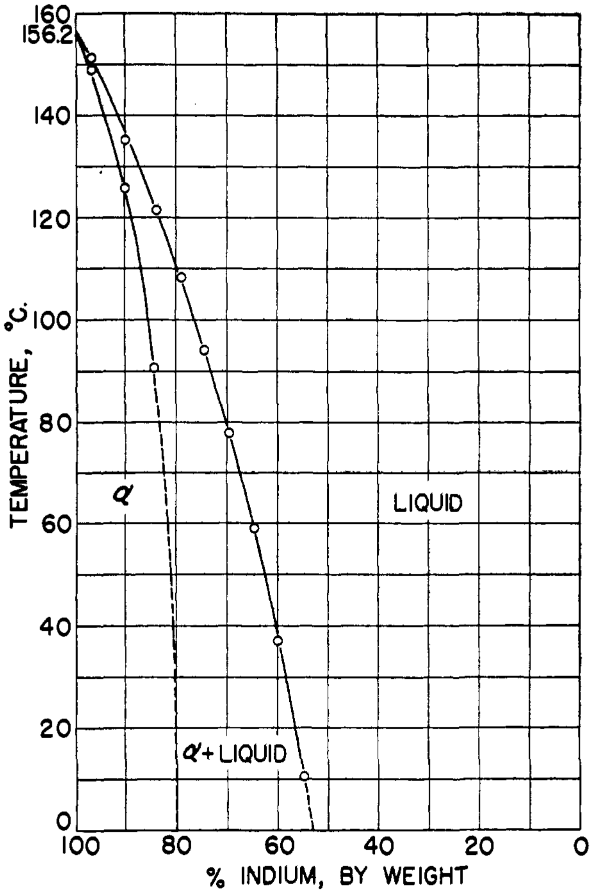

Fig. 1.

The cooling curves indicate that mercury forms a solid solution with indium. The solid solution region is labeled α in Fig. 1.

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The Logarithmic Growth Law for the Oxidation of Titanium

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Two different studies of the oxidation of titanium have led to contradictory interpretations regarding the form of the rate law above and below 350°. Gulbransen and Andrew[1] concluded that a modified parabolic rate law holds throughout the range 250 to 600°, although their Arrhenius plot of the parabolic rate constants shows a change of slope for

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(1) E. A. Gulbransen and K. Andrew, *J. Metals*, **1**, 741 (1949).