

# Activity Coefficients of Mercury in Indium Amalgams

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The mercury vapor pressures of amalgams containing between 5 and 80% indium are measured at temperatures varying between 40° and 100°C by means of Knudsen's effusion method; the correction coefficients, which must be taken into account in this method, are determined by measuring the vapor pressure of pure mercury. Vapor pressure values are used to calculate the mercury activity coefficients.

Two chambers  $V_1$  and  $V_2$ , are connected by a small opening.  $V_1$  contains a vapor at the pressure  $P_1$ , while vacuum is present in  $V_2$ . Knudsen (6-9) has shown that under certain conditions, the measurement of the amount of effused vapor per unit time permits the calculation of the pressure  $P_1$  of the vapor contained in vessel  $V_1$ .

These four conditions are: The opening thickness must be infinitely thin and its diameter must be less than the mean free path of the vapor molecules under the experimental conditions.

The rate of loss in weight by effusion must be negligible compared with the vapor weight in  $V_1$ . In case of a saturating vapor, it is sufficient that the evaporation area of the studied sample should be large compared with the area of the effusion opening.

The temperature of the effusion opening determines the effusion conditions. In case of a saturated vapor, the temperature of the sample and of the effusion opening must be equal.

The coefficient of vapor condensation in vessel  $V_2$  must be equal to unity, and the effusion must be carried out in the best possible vacuum.

$P_1$  is then given by:

$$P_1 = \frac{K}{S} \left( \frac{2 \pi RT}{M} \right)^{1/2} \frac{dm}{dt} \quad (1)$$

$K$  is a correction coefficient, taking into account the actual experimental conditions.

## EXPERIMENTAL

**Apparatus.** The experimental apparatus (Figure 1) consists of a normal vacuum setup whose vacuum limit is  $10^{-6}$  torr, and the effusion apparatus is made of borosilicate glass. It includes four distinct parts: The effusion cell is a cylindrical container (2 cm high, 3 cm in diameter) receiving the sample under study; the effusion opening, 0.23 cm, is situated on the upper part. The amalgam is introduced through a vertical glass tube whose upper part is sealed with two Teflon airtight stopcocks. The air block thus formed permits the filling of the cell under vacuum.

The cell and container together under vacuum are immersed into a globe filled with water at a regulated temperature; the function to the vacuum setup is made under the condenser.

Mercury condensed at the level of the brass ring must be collected into the capillary tube. For this purpose, the pipet containing the capillary tube (2 mm in diameter) is provided at its extremity with a perbunan spatula; it can be moved from the outside through an airtight passage fixed at the lower part

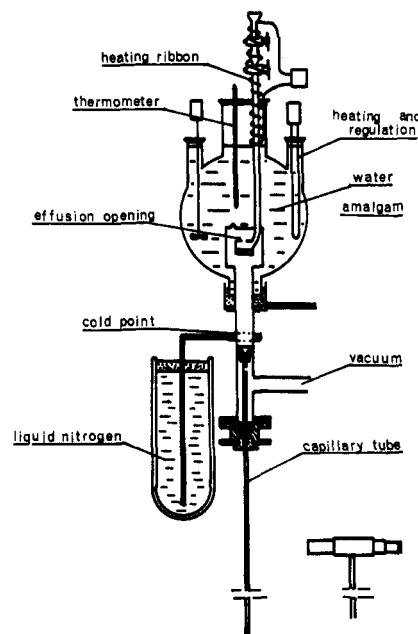


Figure 1. Experimental apparatus

of the apparatus. A sighting apparatus allows the marking of the mercury level with a precision of  $1/10$  mm.

## PROCEDURE

It is absolutely necessary to use products as pure as possible and with accurately known concentrations. The process used to get the amalgam is illustrated in Figure 2. Mercury is let in through the receptacle, 2, which is degassed under atmosphere of argon. The needed quantity of indium is tapped in while maintaining the vessel temperature. The opening, 1, is sealed with a blowpipe, and pumping is done down to  $10^{-6}$  torr. Then the body of the apparatus is separated from the pumping opening and is tipped to an angle of  $30^\circ$  to make the indium flow on the mercury through the opening A. (The narrow neck keeps the grayish stain on the surface of the indium.)

The chamber, 3, is separated at A, and the part, 2, is stirred slightly to aid the mixing. The apparatus is tipped again and the amalgam flows out toward the receiving capsule, 5, which is sealed by melting. From the residuum contained in the chamber, 3, the real percentage of the amalgam is worked out. Washing the effusion apparatus must be done with care;

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Table I. Correction Coefficient *k*

Temp of sample, K	<i>P</i> <sub>2</sub> measured value		<i>P</i> <sub>1</sub> tabulated value		<i>k</i>
	Baryes	10 <sup>-3</sup> torr	Baryes	10 <sup>-3</sup> torr	
373	356.8	268	363	273	1.017
363	206.6	155	210	158	1.016
353	115.9	87	118	88.8	1.018
343	62.3	46.7	64.1	48.2	1.027
333	32.6	24.5	33.5	25.2	1.028
323	16.2	12.2	16.9	12.7	1.043
313	7.73	5.8	8.08	6.1	1.046
303	3.47	2.6	3.69	2.8	1.063

several washings and rinsings are necessary, and they must be followed by a prolonged drying at 150°C.

The filling of the effusion cell, as well as the opening of the bulb of the amalgams, is carried out under a nitrogen atmosphere.

The diameter of the opening must be less than the mean free path of the vapor molecules—theoretically this is always possible. For a small diameter, the height of mercury collected in the capillary tube is too small, and the measuring error is increased.

The chosen diameter is the result of a compromise between these two obligations. At this point, it is to be noticed that the effusion conditions for amalgams are always better than for pure mercury. In fact, the correction coefficient, which must

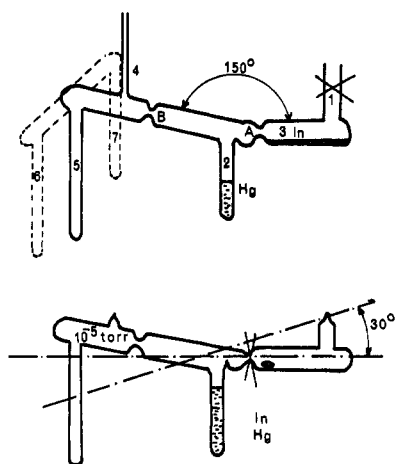


Figure 2. Amalgam apparatus

be taken into account in this method, depends on a mean free path but of geometrical conditions also.

Rather than determine *K* theoretically, which is always difficult, we preferred to gauge the apparatus with pure mercury (2, 3). Table I gives the mercury-vapor pressure value experimentally determined according to the mercury temperature. Practically, the variation *dh/dt* is measured according to time, the height, *h*, of the mercury is collected in the capillary tube, and the vapor pressure is calculated from Knudsen's equation, bearing in mind that:

$$\frac{dm}{dt} = k' \frac{dh}{dt}$$

$$P_2 = \frac{1}{S} \left( \frac{2 \pi RT}{M} \right)^{1/2} k' \frac{dh}{dt} \quad (2)$$

It is thus possible to calculate the value of the correction coefficient, *k*, such as:

$$P_1 = kP_2 \quad (3)$$

where *P*<sub>1</sub> is the tabulated value (11) of the mercury vapor pressure. The values of *k* are indicated in Table I.

### RESULTS

The total vapor pressure over indium mercury amalgams containing up to 80% indium has been measured. In fact, the vapor pressure measured is that of mercury above the amalgam, considering the fact that the vapor pressure of indium is negligible in the field of studied temperatures.

The results are given in Table II. As a comparison, we have indicated the values obtained by Bernier and Efferman (1) and Margolis (10). The measuring error depends on the vapor pressure value—low for higher pressures.

$$\frac{\Delta P_{Hg}}{P_{Hg}} < 0.5\% \text{ for } P_{Hg} = 2.73 \cdot 10^{-4} \text{ torr} \quad (4)$$

It increases when the vapor pressure decreases:

$$\frac{\Delta P_{Hg}}{P_{Hg}} \simeq 2\% \text{ for } P_{Hg} = 6.10 \cdot 10^{-3} \text{ torr} \quad (5)$$

The activity coefficients of mercury in the presence of indium have been determined for the liquid state of amalgam (4) with the equation:

$$P_{Hg} = P_{Hg}^0 \cdot x_i \cdot \gamma_{Hg} \quad (6)$$

where:

*x*<sub>i</sub> is the mercury concentration expressed in mole fraction

Table II. Hg Vapor Pressure Above Indium Amalgam (*P*<sub>Hg</sub>), Activity Coefficient of Mercury in Presence  $\gamma_{Hg}$  of Indium

Amalgam temp, K	<i>P</i> <sub>Hg</sub> <sup>0</sup> (10 <sup>-3</sup> torr)	373		363		353		343		333		323		313	
		<i>P</i> <sub>Hg</sub>	$\gamma_{Hg}$	<i>P</i> <sub>Hg</sub>	$\gamma_{Hg}$	<i>P</i> <sub>Hg</sub>	$\gamma_{Hg}$	<i>P</i> <sub>Hg</sub>	$\gamma_{Hg}$	<i>P</i> <sub>Hg</sub>	$\gamma_{Hg}$	<i>P</i> <sub>Hg</sub>	$\gamma_{Hg}$	<i>P</i> <sub>Hg</sub>	$\gamma_{Hg}$
	% In by wt <i>X</i> <sub>i</sub>	273		158		88.8		48.2		25.2		12.7		6.1	
5	0.92	248	0.99	146	1	82	1	44.2	0.99	23.1	0.99	11.4	0.97	5.6	0.99
10	0.83	218	0.95	129	0.98	72	0.97	39	0.97	20	0.95	9.95	0.94	5.05	0.99
19.2	0.69	177	0.94	99.5	0.91	57	0.93	30.8	0.93	16.5	0.95	8.2	0.93		
30.1	0.57	142	0.91	82.5	0.91	47	0.93	24.7	0.90	12.9	0.9	6.5	0.9		
39.8	0.47	104	0.81	63	0.85	35	0.84	19	0.84	10	0.84	5	0.84		
48.9	0.365	68	0.68	40	0.69	22	0.68	11.9	0.68	6.3	0.68				
60.1	0.276	25.9	0.34	15	0.34	7.5	0.3								
69.9	0.198	13.8	0.25	7.9	0.25	4.4	0.25								
80.1	0.16	12.6	0.28	7.5	0.27										
	0.178														
60		Bernier and Efferman (1)				12.5									
72						12.5									
60		Margolis (10)				6									

and  $P_{\text{Hg}}^{\circ}$  is the vapor pressure of pure mercury at the temperature,  $T$ , under study.  $P_{\text{Hg}}$  is the mercury vapor pressure at the temperature,  $T$ , under study. The variations of the activity coefficient with the temperature are within the range of the precision of the measurements:

$$\left( \frac{\Delta \nu_{\text{Hg}}}{\nu_{\text{Hg}}} \simeq 1-2\% \right)$$

The values of  $\gamma_{\text{Hg}}$  are indicated in Table II. For the solid liquid phase, we used the liquidus curve given by Ito et al. (5). The activity coefficient of mercury in the presence of indium can be considered as independent of the temperature in the range of temperature studied. On the other hand, the dependence as regards the concentration of indium is important and the mercury-indium amalgams deviate negatively from ideality.

## CONCLUSION

The method used has allowed the determination of the mercury vapor pressure of mercury above the indium amalgams with an accuracy at least equal to that of the absorption method. However, under the experimental conditions chosen here, the measuring field is more limited. These results allow the calculation of the temperatures of the walls corresponding to the maximum luminous efficiency of fluorescent lamps containing an indium amalgam. For example, a 60-W fluorescent lamp, with an incorporated amalgam of 80% indium, has an optimum mercury temperature of 87°C, whereas the measured value is 84.5°C.

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## NOMENCLATURE

$M$	=	molecular mass, grams
$m$	=	effused mass, grams
$P$	=	vapor pressure, Baryes or torr
$R$	=	universal gas constant, $8.31 \cdot 10^7$ erg/K
$S$	=	area of the effusion opening, $\text{cm}^2$
$t$	=	time, sec
$T$	=	temperature, K

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# Vapor-Liquid Equilibrium Data for Systems Ethylbenzene—Anisole and *p*-Xylene—Anisole

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**Isobaric vapor-liquid equilibrium data were obtained for the binary systems ethylbenzene-anisole and *p*-xylene-anisole at 760 mm of Hg pressure. The *t*-*x*-*y* data for these systems were tested for thermodynamic consistency. The experimental phase compositions were compared with those calculated by Raoult's law**

This work forms part of a program on the evaluation of non-ideality characteristics for mixtures of close-boiling hydrocarbons and other types of compounds. Vapor-liquid equilibrium data were determined for the systems ethylbenzene-anisole and *p*-xylene-anisole at 760 mm of Hg pressure.

## EXPERIMENTAL

**Materials.** Ethylbenzene, laboratory reagent grade, obtained from British Drug Houses, Poole, England; *p*-xylene,

pure grade, obtained from Riedel-De Haen AG, Seelze-Hannover, Germany; and anisole, pure grade, obtained from W. G. Bush and Co., London, were dried over anhydrous calcium chloride and further purified by distillation in a 30-mm glass column packed to a height of 1 meter with 4-mm helices made from Nichrome wire. The column was provided with an air jacket and a 125-W heater to minimize heat losses and run at total reflux for 30 min, and the low-boiling impurities were drawn off as rejects at a very low rate. When the desired boiling temperature was attained and remained constant for 15 min, the fraction was collected and near total reflux conditions were maintained until the contents of the distillation flask were reduced to about one

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