Vapor-Liquid Equilibrium Still for Use at 1 mm. Hg Pressure

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Vapor-liquid equilibrium stills especially designed for use at low pressures (1 mm. Hg or less) are not frequently found in the literature. Williams (*8*) described one such apparatus for use at 1 mm., and Perry and Fuguitt (*6*), one for use at 0.1 mm. pressure. Neither of the two, however, allows for measurement of boiling point and both belong to the category of vapor phase circulating stills that often have the disadvantage of not allowing sufficient time for mixing of the circulating lighter phase with the boiling liquid. Malyusov et al. (*3*) have worked with a still of their own design, down to 0.0001 mm. pressure, a low pressure which calls for a very complicated design.

An attempt was therefore made to design a new still for use at 1 mm. Hg pressure or less, incorporating such advantages as ease of use and construction and smooth operation. The still, in operation for some time now, has given satisfactory results. The description of the apparatus and some of the data gathered are presented here.

EXPERIMENTAL PROCEDURE

Equilibrium Still

In the apparatus, shown in Figure 1, a mixture of the vapor and liquid phase is recirculated to the still. The system might be classified as an "Othmer-type still" with two modifications, a directly superimposed condenser as has already been used by Othmer et al. (*5*) and external heating coils as were applied also by Othmer and coworkers (*4*). The apparatus consists of a boiling chamber, a condenser, vapor and liquid samplers, and four circulating coils.

Liquid is charged to the still through the inlet *G*. The heating is done externally by the use of four electrical heaters installed within the coils (only two shown in the figure). The liquid, which fills the lower part of the apparatus, eventually comes to boiling within the coils and is discharged into the chamber. Here equilibrium between the two phases is attained, the vapor condensing in the condenser. The condensed vapor phase goes through the drop counter to the vapor sampler *E*. From here the liquid reaches the mixing chamber where it mixes with the liquid coming from the liquid sampler *F*. The mixture is then recirculated to the still owing to the difference in densities originated by the heating in the coils.

To insure proper mixing in the evaporating chamber, the entrance tips from the coils make an angle of roughly 30 deg. with the inner wall, a design that induces a circular movement of the boiling liquid. Bumping is thus completely eliminated.

The other possible difficulty, the hydrostatic effect, was investigated by the use of a third sampler (not shown in the figure) which takes liquid from about 1 cm. under the free boiling surface. This permits the comparison of the concentration at this point with the one given by sampler *F*. The difference between the two molar fractions was never higher than 0.001.

Temperature is measured by means of two ASTM mercury thermometers with a precision of ±.05°C. for which two thermowells are available: one at *H*, the other being inserted through G once the still is charged.

The heating system consists of four independent heaters made of Cronifer III wire, 0.30 mm. in diameter, with a total power of 400 w. An additional heater of 100 w. is wound on the reboiler and the mixing chamber as well as on the tubes connecting the samplers with the mixing chamber. These heaters, whose purpose is to balance heat losses and to favor circulation from the samplers, are independently controlled. The whole apparatus is insulated, with thermocouples inserted between the insulation and the glass at certain points where a control of the outer temperature of the still was found necessary, mainly in the mixing chamber and the reboiler.

Control of the pressure is achieved by the usual arrangement: vacuum pump, surge tank, solenoid valve, pressure controller, and manometer.

When working at 1 mm. Hg pressure, the controller used was the Speedivac vacuum switch in the range of 0 to 20 mm. and pressure was read in a McLeod manostat, with a range of 0.01 to 10.0 mm. At the higher pressure, 200 mm., the controller was a Vacutrol manostat of J. F. Scanlon with a closed U-type manometer.

To prevent eventual entrainment of the oil of the vacuum

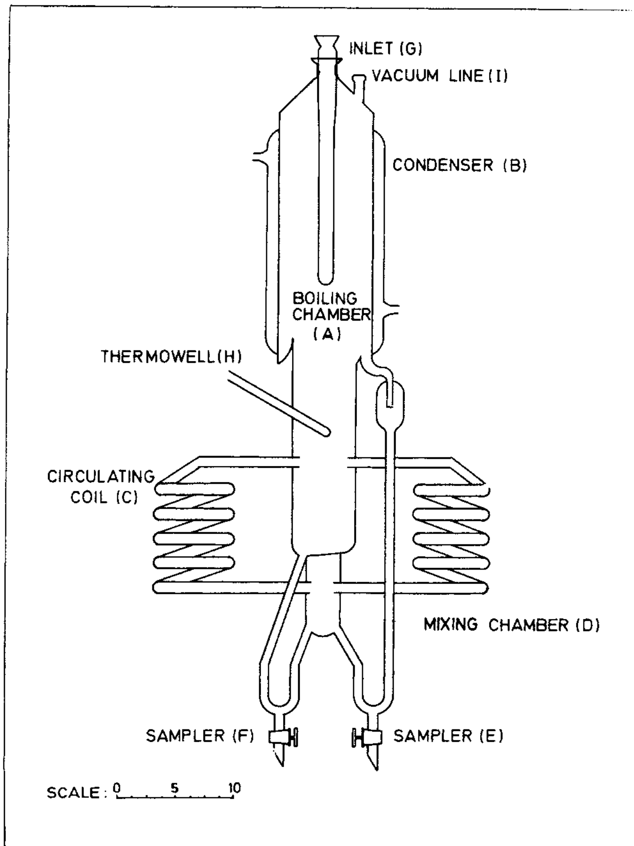

Fig. 1. Equilibrium still.

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pump into the system, oil and vapor traps are used at appropriate points. Equilibrium was achieved in less than 1 hr. As can be seen from the figure, the bottom of the still is slightly inclined for draining purposes.

Equilibrium Data

The still was run at 200 mm. and 1 mm. Hg pressures. The system ethylene dichloride-toluene was chosen for use at 200 mm. while the di-*n*-butyl phthalate—di-*n*-butyl azelate mixture was used at 1 mm. The ethylene dichloride, toluene, and di-*n*-butyl phthalate were commercial products purified by fractionation through a 20-plate distillation column at 200 mm. Hg (the first two products) and 1 mm. Hg (the di-*n*-butyl phthalate). The di-*n*-butyl azelate was prepared according to the method described by Williams (*8*). For the two systems refractive index was used to measure sample concentrations.

Equilibrium data for the system ethylene dichloride-toluene at 200 mm. Hg pressure are presented in Figure 2. This mixture acts ideally as has been shown by Jones et al. (*2*). In the figure, the solid line has been drawn from data as predicted by Raoult's law. Toluene vapor pressure was calculated (*7*) by means of

$$\log_{10} P^\circ = 6.95464 - 1344.800/(T + 219.482)$$

RESULTS

As can be seen in Figure 2, agreement of experimental data with theory is satisfactory. This and the fact that the apparatus showed a good performance at 200 mm. Hg pressure allowed for experimentation to be carried out at a lower pressure.

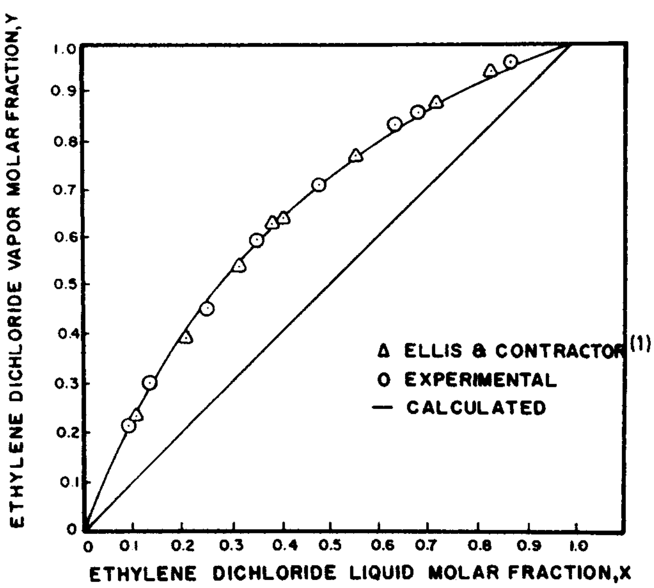

Fig. 2. System ethylene dichloride-toluene; vapor liquid equilibrium at 200 mm. Hg.

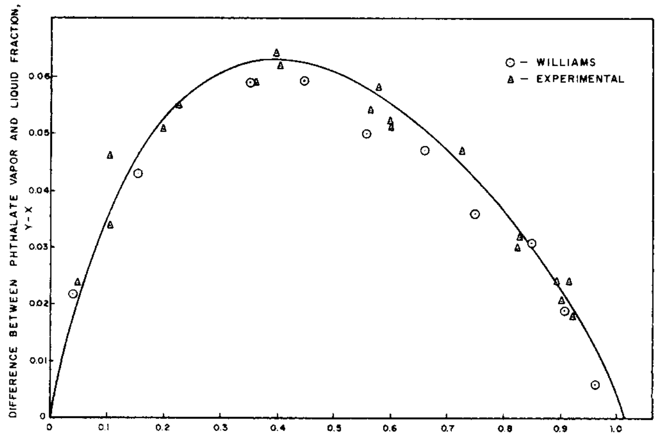

Fig. 3. System di-*n*-butyl phthalate—di-*n*-butyl azelate; scattering of vapor liquid equilibrium data at 1 mm. Hg.

Table 1. Equilibrium Data for the System Di-*n*-Butyl Phthalate—Di-*n*-Butyl Azelate

(Pressure: 1 mm. Hg.)

Temperature °C.	Molar fraction di-*n*-butyl phthalate Liquid	 Vapor
154.6	0.000	0.000
154.0	0.048	0.072
154.0	0.103	0.149
153.5	0.105	0.139
153.0	0.195	0.246
153.2	0.223	0.278
152.2	0.358	0.417
152.1	0.393	0.457
151.4	0.400	0.462
151.0	0.557	0.611
150.4	0.593	0.645
150.3	0.595	0.646
150.0	0.716	0.763
149.5	0.813	0.843
149.6	0.817	0.849
148.5	0.881	0.905
149.0	0.891	0.912
148.8	0.905	0.929
148.8	0.914	0.932
147.9	1.000	1.000

The still was actually intended for use at 1 mm. pressure or less. Data for the system di-*n*-butyl phthalate—di-*n*-butyl azelate at 1 mm. are presented in Table 1 and Figure 3, which shows the variation of the difference in molar fractions for the vapor and the liquid versus the molar fraction of the liquid. On this figure Williams' (*8*) data for this mixture are reported, while the full line has been drawn assuming ideal behavior. For the vapor phase, the ideality assumption is based on the low pressure while for the liquid phase it stands on the similarity of the two compounds. By smoothing experimental data collected with this apparatus, the vapor pressure of di-*n*-butyl phthalate is predicted as

$$\log_{10} P^0 = 0.02608\ (T + 273.2) - 11.006; \quad (147.9 \leq T \leq 154.6°\text{C.})$$

Full agreement was found among experimental data, Williams' results, and theoretical prediction based on ideal behavior. This is considered to be a sound proof of the thermodynamic consistency of the data. It seems highly improbable that, had the mixture been nonideal, the same systematic error would have been present both in this work and in Williams' so as to balance the theoretical error.

It must be realized that even a small experimental error will show greatly in the results for a system such as the present one, with only 7°C. difference in boiling points. Experiments were carried out with great care and for more points than in the previous case. Again, as was the case for the higher pressure, boiling was smooth and no bumping was noticed.

In addition to being useful for high vacuum studies, the apparatus should be advantageous at higher pressures for systems with a wide deviation of boiling points, such as ammonia and water. This could be the subject for further experimentation.

SUMMARY

A new vapor-liquid equilibrium still was designed and constructed which features simple design, smooth per-

formance, and short equilibrium time. The apparatus was tested at 200 and 1 mm. Hg pressure, giving entirely satisfactory results at both pressures.

ACKNOWLEDGMENT

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NOTATION

P^0 = vapor pressure, mm. Hg
T = temperature, °C.

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Kinetics of Ethylene Oxidation on a Supported Silver Catalyst

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Since Lefort's original description of the process in a patent issued in 1931 (*1*), the oxidation of ethylene to ethylene oxide on a silver catalyst, with concurrent formation of carbon dioxide and water as by-products, has been extensively studied. Although much fundamental work has been done, uncertainties remain concerning the effects of reactant concentrations and the nature of the species adsorbed on the catalyst. Contradictions are apparent when the results of adsorption studies on silver are compared with conclusions based on models of the reaction kinetics. Furthermore, the mode of action of moderators and promoters is still not well understood. The purpose of this work was to obtain accurate kinetic data over a wide range of reactant concentrations and to provide some insight into the mechanism of the reaction.

SUMMARY OF PREVIOUS WORK

Several reviews of catalytic oxidation have been published recently (*2* to *5*), and an extensive review is given in the thesis by Klugherz (*6*). Only certain studies on adsorption and kinetics are reviewed here.

Adsorption

The chemical composition of the catalyst must first be considered. At 220°C. the equilibrium pressure of oxygen in a silver oxide-silver system is 2.7 atm. (*7*, *8*), and the oxide phase cannot exist at the conditions usually used for ethylene oxidation studies. Most adsorption studies have been concerned therefore with the interaction of various gases with silver. Only recently has it been recognized that even though silver oxide does not exist as a separate phase at reaction conditions, its properties as an adsorbent should be investigated.

Oxygen adsorption on silver has been studied most extensively. Both kinetic and equilibrium measurements have been made, and oxygen is known to be fairly strongly chemisorbed in at least two different forms. However, the nature of these species is still in doubt. Some investigators, such as Smeltzer et al. (*9*), Ostrovskii and Temkin (*10*, *11*), and Czanderna (*12*), believe that atomic and molecular oxygen species exist on the surface. Others, such as Sandler and co-workers (*13*, *14*), believe that both adsorbed species are oxygen atoms which differ only in their binding energy. Based on measurements of oxygen

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