

tion is probably similar to that put forward by Christiansen and Kramers⁴ to explain a simpler type of pseudo-unimolecular reaction. In this theory an activated molecule is formed for every one that reacts.

Benzoyl peroxide acts as a trigger catalyst in starting reaction chains and is itself destroyed in the process, since chemical tests always showed its absence when the catalyzed reaction stopped. Anti-catalysts, like sulfur, interrupt the reaction chains. The inhibition of the reaction by toluene may be explained on the basis that activated molecules give up their energy to the toluene molecules before they can combine with other vinyl acetate molecules. In other words, the toluene has the same effect in breaking reaction chains that walls exhibit in some homogeneous gas reactions.

Summary

The polymerization of pure vinyl acetate is shown to follow the unimolecular rate law. In toluene solution the rate of reaction is retarded. The kinetics of the polymerization are explained on the basis of a chain reaction. Benzoyl peroxide acts as a trigger catalyst by initiating reaction chains. Sulfur inhibits the reaction.

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THE VACUUM FRACTIONATION OF PHLEGMATIC LIQUIDS

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In the course of some work on heavy oils the need has been encountered for an adjective which will convey the sense of "difficultly volatile" or "high boiling." Instead of inventing a word we have prepared to adapt a word which is already well known and, therefore, nearly self-explanatory. Such a word is "phlegmatic." Derived from the Greek *φλεγματικός*, the original suggestion of "fieryness" has given place to the well-accepted sense of sluggishness, apathy or resistance to disturbance. *Phlegmatic* seems a particularly suitable word to denote high-boiling properties, and it is the adjective which will be used throughout this paper.

Many separations of phlegmatic liquids by fractional distillation could be performed more efficiently or more conveniently¹ at very low pressures if it were not for the uncertainty concerning the real pressure in the distilling

⁴ Christiansen and Kramers, *Z. physik. Chem.*, **104**, 451 (1923). See also Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Clarendon Press, Oxford, 1929, Chapters V and VI.

¹ Bumping vanishes entirely at pressures below 1 mm.

apparatus. Where simple distillation is concerned, without reference to the temperature at which it occurs, high vacuum can be employed.² Where the temperature-pressure relation is important, as it is in fractionation, or in determining the purity of a distillate, or in identifying a material by its boiling point, then relatively poor vacua have hitherto been compulsory. It is safe to say that any boiling point recorded in the literature from ordinary distillations at 10 mm. is probably inaccurate by 1°, and boiling points expressed at lower pressures are completely unreliable.

This unreliability is due chiefly to the lack of uniformity of pressures in the distillation apparatus. In using gaseous systems at atmospheric pressure it is usually assumed that the pressures are identical at all parts of the apparatus; a gage attached at any part will give information relating to the whole. Where the internal conditions are dynamic rather than static, owing to a flow of gases from one portion to another, the pressures no longer are equal in all parts, a difference of a millimeter or so arising in the effort necessary to move the gases. The difference may be less than one-tenth of one per cent. of the total pressure, and is usually neglected. Under high vacuum conditions a difference of one millimeter may cause a difference of a

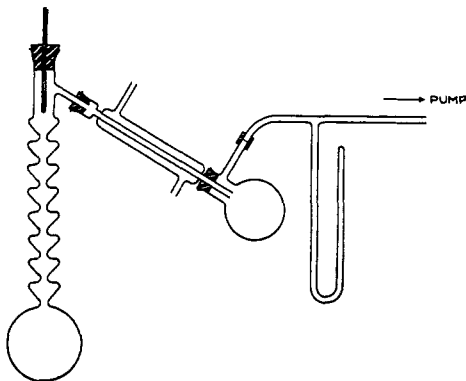


Fig. 1.

thousand magnitudes in the density of gases in various parts of the system. Measurements of vapor tension taken at an appreciable distance from the thermometer region may be entirely untrustworthy.

A full discussion of the factors contributing to false pressure readings has been given in a previous paper.² It will be more useful now to recall the phenomena which usually occur during the low pressure distillation of an organic liquid in the conventional distilling flask and condensing arrangements. In Fig. 1 a flask with rectifying column is shown connected by a side tube with a water-cooled condenser, a receiver, a manometer and an exhaust pump; a thermometer projects into the rectifying column to just below the exit tube.

We will place in the flask some comparatively phlegmatic liquid and commence distilling at a reduced pressure. A good material to distil would be butyl benzoate. With the pressure at 60 mm., vapor would pass over excellently at 170°. At 20 mm. the thermometer would register 132°; at 10 mm. 117°; at 5 mm. 104°; at 3 mm. 97°; at 1 mm. 92° and at

² Hickman and Sanford, *J. Phys. Chem.*, **34**, 637 (1930).

0.0 mm. 90° . Now it is apparent that if the temperature–pressure relation which subsists from 60 to 10 mm. still holds, as we have every confidence that it does, the temperature at 0.0 mm. pressure should be about absolute zero. The usual mercury manometer cannot be read with the naked eye below 0.1 mm., but even at this pressure the boiling point of butyl benzoate should be less than 50° . Furthermore, the discrepancy in boiling point is not constant. If, with the manometer still reading substantially zero, the heat is increased under the distilling flask, the mercury in the thermometer may rise 5 or 10° ; if the heat input is decreased, it will fall.

The temperature measurements, within limits, are beyond reproach, but the pressure measurements are faulty. If the thermometer registers

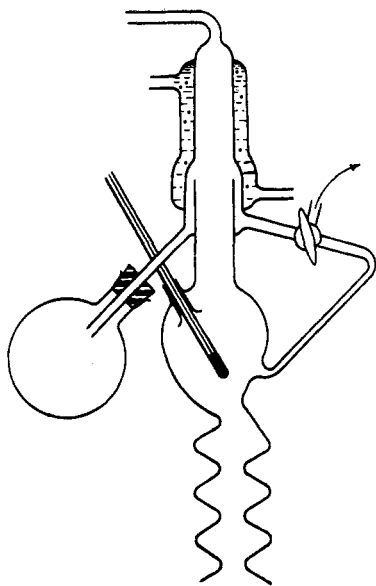


Fig. 2.

60° , the pressure of a saturated vapor of butyl benzoate around the thermometer bulb must be about 1 mm. This vapor then passes into the condenser and turns into liquid in equilibrium with a vapor at such negligibly small pressure that for our present purposes it is zero. More vapor from the flask continues to flow into this empty space, and the temperature at the thermometer of 60° is a measure of the pressure (1 mm.) which is necessary to force the quantity of vapor which survives each moment, into the passage from the flask, through the side tube and into the condenser. Supply more heat at the flask, and the pressure must rise to drive over the larger quantity of vapor.

Many partial remedies will occur to the reader but drastic alterations to the equipment are required for a complete cure.

Two conditions should be satisfied if the data are to be recorded correctly. The thermometer should be placed in an expansion of the column where the vapor has a relatively small velocity, and the manometer should operate directly from the wall of this expansion. No passage filled with gas can communicate the pressure with an outside gage unless this passage and the pressure recording mechanism at the end of it are kept at the same temperature as the bulb.

It is simpler, therefore, to use a small portion of the condensate as it flows down the walls of the bulb as a manometric fluid and to provide a glass tube and recording scale at a convenient point on the bulb. The pressure side, however, is only one-half of a manometer, and it is necessary to pro-

duce a substantially perfect vacuum at the other end.³ This would mean, since the filling is to be of the material distilled, that the high vacuum must be applied whenever wanted, presumably by a separate pump. The complication can be avoided by forming the condenser into a simple condensation pump, so that the vapor under treatment produces its own reference vacuum. We have given a still head (Fig. 2) modeled in this manner prolonged trial in the laboratory and have found that with liquids of the class for which it was intended the head never failed to yield a better reference vacuum than could be communicated through the three-way stopcock from a separate pump.

The differing capillary actions at the ends of the self-contained manometer require that the zero point be found empirically by momentarily relieving the vacuum so that the liquid may equalize in the two limbs. The liquid in the automanometer requires scavenging frequently if the condensate varies in volatility or density as distillation proceeds.

The still head can act as a diffusion pump only if the pressure at the exit tube to the exhaust pump is considerably less than the pressure of vapor in the thermometer cavity and thus at the male jet. It is therefore quite essential to have a sensitive manometer in the exhaust line. A McLeod gage and possibly a Pirani gage could be used, but we favor a direct reading liquid manometer. The mercury manometer is unreliable because of difficulty of reading minute changes in level and because of the doubt which must al-

ways exist as to the perfection of the reference vacuum in the closed limb. We have devised a butyl phthalate filled manometer which, although of somewhat complicated design, is simple and entirely reliable in use. It is illustrated in Fig. 3 and is described in an appendix to this paper.

³ If the temperature of the liquid in the vacuum end is 80° less than at the pressure end, the vapor pressure will generally have decreased a thousand times and may be neglected. In chemical vacuum work it is a useful rule that any liquid which is under distillation may itself be used cold as a manometric fluid, as a joint seal and as a film to prevent the escape of volatile matter from the inside of rubber pressure tube and from corks. We repeatedly perform distillations in special apparatus at 0.1 micron using matured rubber stoppers and rubber tubes soaked in the phlegmatic liquid under treatment.

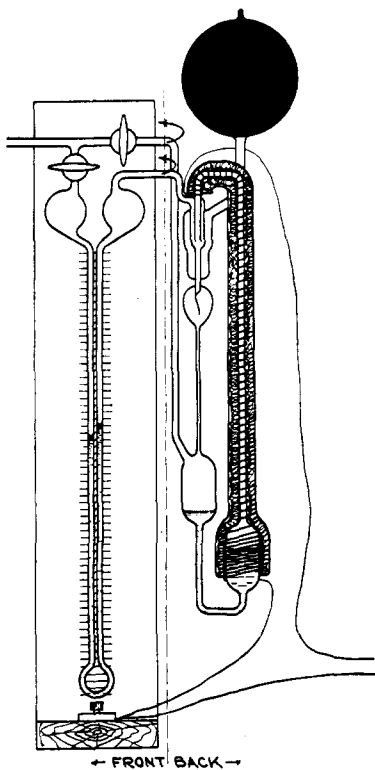


Fig. 3.

The condensation still of Fig. 2 will only accommodate vapor pressures up to 1 mm. and liquids to be condensed at 10 and 20 mm. will not generally survive on the high vacuum side of the jet unless the condenser is maintained many degrees below zero centigrade. It then becomes convenient to operate with a positive air pressure in the system and attach an external phthalate manometer to the free arm at the three-way stopcock of Fig. 2.

The pressure difference between the thermometer cavity and the condenser is then added to the pressure registered by the external manometer and the sum is the pressure at which the liquid is condensing.

A very convenient unit for the accurate distillation of small samples ranging from 5 to 100 g. is that shown in Fig. 4. The thermometer bulb hangs in the largest cavity of the dephlegmating column and a side manometer tube passes from the lower region of the cavity to the top of the condensing chamber. The latter may be water cooled, but it is generally sufficient to employ the draught from a small fan. The condensate collects in the annulus and flows out of the delivery tube to the left. The correct boiling point at regions of rapid change of boiling point can be secured by preventing the distillate from escaping. It then collects in the annulus and flows back down the column. When the boiling point has been secured the side tube is unclipped and collection of the distillate resumed. Care must be taken that the cool distillate does not run down the thermometer bulb from the annulus. The pressure in the thermometer cavity is, of course, the sum of the pressure in an external manometer and in the automanometer.

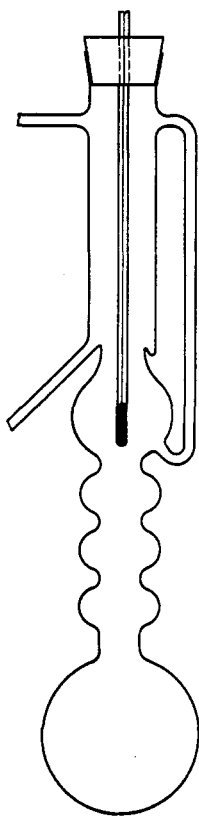


Fig. 4.

The measurement of pressure by an external manometer becomes more and more accurate as the cavity housing the thermometer and the passage therefrom to the condenser become larger. We thought, at one time, that the automanometer construction could be abandoned in lieu of another suitable design. It was soon found that very large openings allowed the vapor-air junction to oscillate in position, at one moment leaving the thermometer uncovered, at another heating the stem many centimeters up. The apparent boiling point would fluctuate correspondingly. It was preferable to confine the vapors in the cavity and allow them to issue into the vacuum system under a small positive pressure. The vacuum system then became a comparatively inexhaustible reservoir waiting to receive products of decomposition or traces of volatile solvents. A much smaller

vacuum bottle could be used in series with the pump to steady the pressure.

It may be inquired which of the columns described is the most useful. Our first choice would be the device pictured in Fig. 3. It may be noted that the point of novelty on which this paper is based is the application of a side tube near the thermometer region of any distilling flask. If the glass blowing difficulties are found insurmountable, quite good work can be done with the simple set-up pictured in Fig. 5.

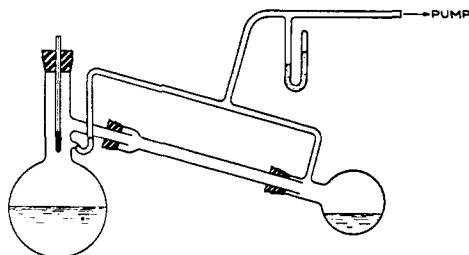


Fig. 5.

Experimental

Distillations were performed in flasks of the type shown in Fig. 1. Two flasks were used, one with a side arm of usual bore, and one with a side arm of as large diameter as the neck of the flask itself. Butyl benzoate was employed as the liquid, and was boiled by an electric heater at three different wattage inputs. The boiling points at each apparent pressure, as registered by an external manometer, are recorded in Table I. The real boiling points corresponding to the recorded pressure are included for comparison and all the data are summarized in Figs. 6 to 8. It will be noticed

TABLE I
DISTILLATION DATA
Boiling points in °C.

Type of still	Watts input	Pressure, mm., in condenser, read by phthalate manometer							Distillation rate, drops per min.	
		20	10	5	3	2	1	0.03		
Fig. 1, small side arm	40	131.6	116.8	104.4	98.8	95.8	95.8	95.2	30, start; 47, finish	
	50	132.0	117.3	106.2	102.8	102.4	101.5	100.0	60-80	
	60	132.3	117.8	107.9	106.5	106.5	69-95	
Fig. 1, large side arm	40	131.6	116.7	102.9	97.4	92.2	85.8	84.8	...	
	50 ^a	132.0	117.4	104.0	99.2	92.9	90.5	90.4	...	
	60	132.8	117.0	103.1	99.4	94.0	88.7	88.1	...	
Fig. 3, condensation still	Variable to keep distn. rate const.	131.5	116.0	102.5	93.0	86.5	75.5	67.8	70	
	At	At	At	At	At	At	At	At	...	
	watts	135	110	99	95	87	70	60	...	
True pressures in condensation still, thermometer cavity		20 mm.	10.01	5.02	3.05	2.07	1.14	0.65	...	
True boiling points at the pressures in the top of horizontal column		...	131.5	116.0	102.5	92.8	86.0	74.3	24.7	...

^a An interval of ten to fifteen minutes was allowed after each adjustment of heat input to allow a steady distillation rate to be reached. In the case marked with the *a* readings were taken after a few minutes only. Their divergence from the other series shows how sensitive to external conditions are these low-pressure distillations.

that the true boiling point of 131.5 at 20 mm. was disturbed by less than a degree at reasonable rates of distillation. A maximum discrepancy of a degree and a half occurred at 10 mm. pressure but the errors became serious at 5 mm. The large side arm flask gave an average inaccuracy of 5° at 3 mm., and the readings were valueless below this pressure. The narrow arm flask failed substantially at 5 mm.

As a second exercise, a sample of commercial α -chloronaphthalene was distilled in the still of Fig. 3. The sum of the pressures in the external manometer and the automanometer was kept at 10 mm. This ensured a pressure of exactly 10 mm. in the thermometer cavity.

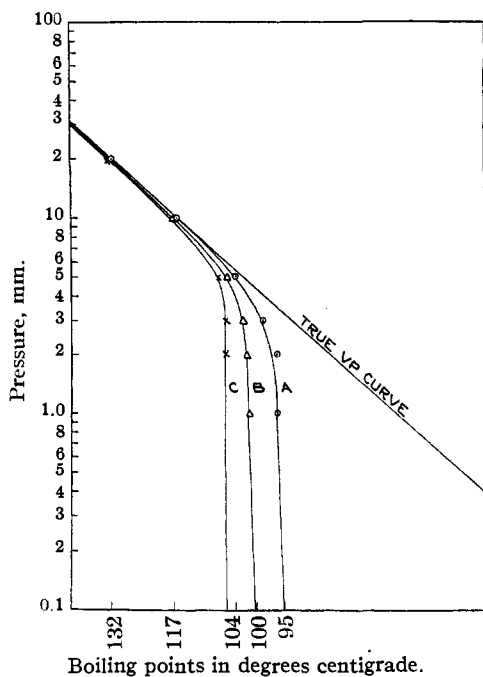


Fig. 6.—*n*-Butyl benzoate. Type of still, Fig. 1, small side arm. A, 40 watts; B, 50 watts; C, 60 watts.

The variation of temperature with the progress of distillation is shown in Fig. 9. It will be noticed that the points fall very smoothly on the curve drawn through them, indicating that little difficulty was encountered in obtaining true readings. The steep rise at the end of distillation is significant. The rise had to be accompanied with a corresponding increase of heat input to keep the pressure constant in the automanometer. Had the distillation been performed in an ordinary flask the real great rise in boiling point of the later fractions would have yielded a small apparent

rise and the rate of distillation would have diminished until the pressure in the thermometer region had fallen sufficiently to convey the more phleg-

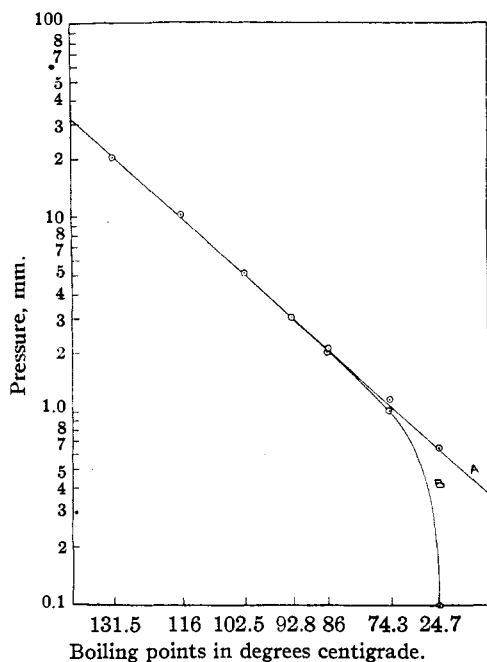


Fig. 7.—*n*-Butyl benzoate. Type of still, Fig. 2, condensation pump. Curve A, pressure read from external manometer plus pressure in automanometer, giving true pressure-temperature relation. Curve B, external manometer readings, yielding false pressure-temperature relation.

matic vapor over with the same heat content. No indication of this would have been visible at the external manometer.

TABLE II
EXPERIMENTAL DATA

True pressure = sum of external manometer readings + automanometer readings	External manometer readings	Automanometer readings, corrected to mm.	Temperature, °C.
10	6.65	3.35	118.9
9	5.65	3.35	116.1
8	4.65	3.35	113.4
7	3.65	3.35	110.3
6	2.65	3.35	107.2
5	1.65	3.35	103.2
4	0.65	3.95	98.7
3	.05	2.95	93.8
2	.05	1.95	85.8
1	.05	0.95	71.3

The composition of the distillate was fairly constant from 20 cc. to 40 cc., and as a further exercise the material was returned to the flask and distillation recommenced until 30 cc. had passed over. A by-pass tube was then inserted so that distillation could proceed cyclically, the material condensing being allowed to flow back into the still. The variation of boiling point with alteration of pressure was then examined and the data re-

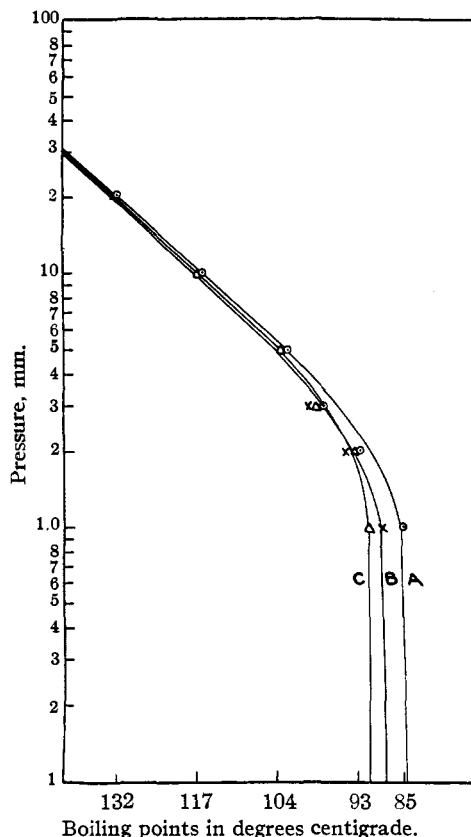


Fig. 8.—*n*-Butyl benzoate. Type of still, Fig. 1, large side arm. Curve A, 40 watts; B, 50 watts; C, 60 watts.

corded in Table II. Figure 10 shows the correct and incorrect pressure-temperature curves drawn from these data. The bent, incorrect curve is the one which would ordinarily have been obtained if the automanometer device had not been employed to correct the pressures read by the external manometer.

It would be impressive to perform a separation of two liquids under vacuum in an ordinary distilling flask and then show the improved result

by using our special apparatus, but after the ample proof of discrepancy which we have already given such a course seems hardly worth while. Instead, a separation of two liquids, butyl benzoate and ethyl phthalate mixed in equal proportions, has been made in a flask with a *wide side* tube (Fig. 1, and Table I, subdivision 2), and this separation has been compared with that obtained with the condensation still of Fig. 2. The wide side tube still was operated with 0.1 mm. pressure in the condenser first at constant voltage input (Curve A, Fig. 11), and then at an attempted constant distillation rate (Curve B), but no steady thermometer readings could be obtained. An absolutely constant distillation rate was difficult to

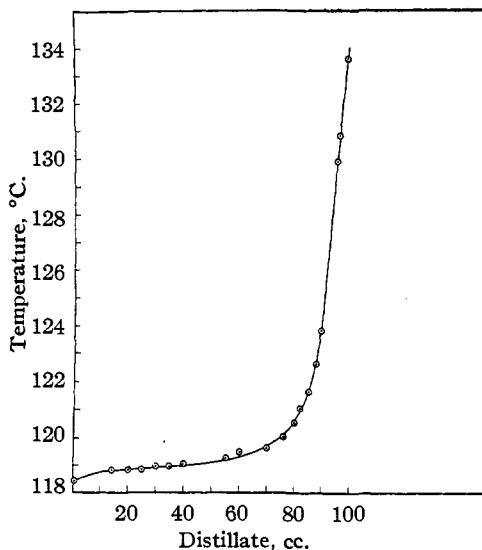


Fig. 9.— α -Chloronaphthalene, 10 mm. of mercury.

secure, and the slightest variation altered the thermometer readings by many degrees. The false maximum at 80 cc. is due to this cause. At 10 mm. (Curve C) better results were obtained. The excellent separations secured at 0.65 mm. and at 10 mm. in the condensation still are shown in Fig. 12. The temperatures are as concordant at a fraction of a millimeter as at 10 mm. The operator would have no difficulty in deciding where to make cuts or what the exact temperature-pressure relation was at each cut.

As a final exercise, about fifteen organic liquids were distilled which had boiling points ranging from 60 to 200° at less than 20 mm. pressure. The samples showed boiling points which were, in general, considerably lower than those stated in the literature.

Further Considerations.—The fall of pressure existing at the jet is not the only pressure difference within the still during distillation. At

each constriction in the dephlegmating column there is a readily measurable drop in pressure which may give useful information. The early experimental column of the type shown in Fig. 2 had six manometers and corresponding thermometers inserted, but was later abandoned in favor of a distillation unit with only three thermometers: One in the liquid in the boiling flask,

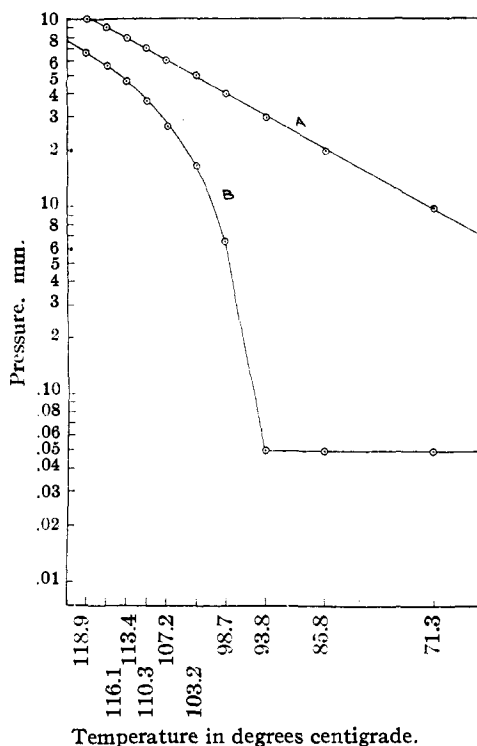


Fig. 10.—A, true temperature–pressure relation obtained by plotting the true pressures (sum of external manometer readings and automanometer readings) against the reciprocals of the absolute temperature. B, false temperature–pressure relation obtained by plotting the apparent pressures (external manometer readings) against the reciprocals of the absolute temperatures.

one in the lowest bulb of the column, and the third in the top bulb before the condensation head. Differences in reading between the bottom and middle thermometer indicated the purity of the liquid, while the top and middle thermometers coupled with manometer readings gave, when plotted with pressures against inverse of temperature, a good indication of the slope of the vapor-pressure curve for each fraction.

In the general reaction $Aa + Bb = AB + ab$ where AB is a much larger

molecule than *ab*, it is unlikely that either *Aa*, *Bb* or *ab*, will have the same slope of vapor pressure curve as *AB*, which will often be steeper, showing a greater depression of vapor pressure as the temperature falls. It is therefore an advantage to have a sheet of graph paper at hand while distilling, and plot the two or three pressure-temperature points for each fraction. The divergence in slope of the connecting lines will show whether a

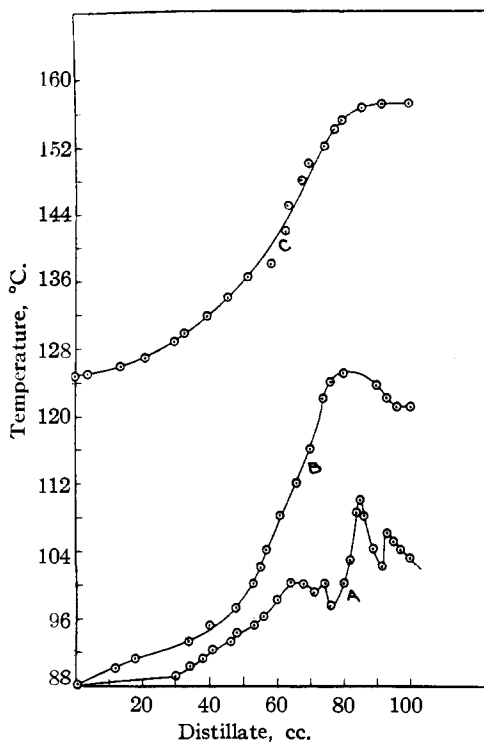


Fig. 11.—Mixture of *N* butyl benzoate + ethyl phthalate, type of still, Fig. 1, large side arm. A, at 0.1 mm. Hg heat input was held constant throughout; B, at 0.1 mm. Hg heat input variable, distillation rate constant; C, at 10 mm. Hg heat input was held constant throughout.

better separation is likely to occur when the pressure is raised or when it is lowered. Often the separation is better at the lowest pressures.

The purification of commercial butyl phthalate is a case in point. The likely impurities are butyl alcohol, butyric acid, phthalic anhydride and butylphthalic acid. At pressures above 20 mm. a constant-boiling mixture distills, which, although it contains over 90% of butyl phthalate, is useless for vacuum pump purposes. When the distillation is performed at

0.64 mm. the butyl alcohol and butyric acid are sucked into the pump, the phthalic anhydride, which now boils at a lower temperature than the phthalate, deposits in a crystalline mass in the condenser, from which position it may be washed down with the first runnings of phthalate. A large middle fraction of pure butyl phthalate comes over, leaving a residue of butyl phthalate and butylphthalic acid which could be worked up under a lower pressure were it not that the crude phthalate is less expensive than the labor involved.

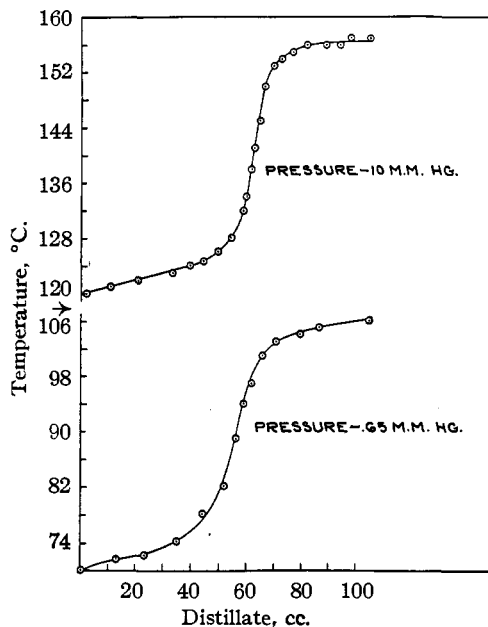


Fig. 12.—Mixture of *n*-butyl benzoate and ethyl phthalate, type of still, Fig. 3.

The statement that the phthalate was distilled at 0.64 mm. is derived from a knowledge that the specific gravity of *n*-dibutyl phthalate is 1.014 at 25° and that the column in the manometer attached to the thermometer cavity was 8.5 mm. high, whence

$$\frac{1.014 \times 8.5}{13.5} = 0.64 \text{ mm.}$$

A convenient way to describe the boiling point of any pure liquid would be in terms of the vapor pressure needed to support a unit height of a column of its own substance. Thus, butyl phthalate boils at 138° at a pressure supporting a column 8.5 mm. high of liquid butyl phthalate. We can denote this pressure by some convenient term, such as auto-pressure, and use the abbreviation A. P. Butyl phthalate boils at 138° at 0.64

mm., or 138° at 8.5 mm. A. P. Such a system of nomenclature would allow the pressure of any homogeneously boiling liquid to be described in conveniently-sized length units which are repeatable by anyone else without reference to tables. For conversion to the common mercury pressure scale, it is necessary to know the specific gravity of the liquid. Part of any pure preparation may be reserved for such a determination. A convenient means for securing approximate information of sufficient accuracy for the work is shown in Fig. 13. Distilled water and the liquid are placed, one in each cup, and slight suction applied by the rubber ball. The liquid rises to a characteristic height which may be compared with the height of the water column. The menisci at the lower ends of the U-tubes compensate for surface tension errors.

We have encountered an interesting source of error. As the liquids become very pure the surface tension alters and the liquid may cease to wet glass. Certain samples of benzyl phthalate appeared to suffer a sudden diminution of vapor tension. The liquid receded in the manometer and the meniscus flattened, occasionally becoming convex like mercury. Touching the tube with a lighted match caused the liquid to flow evenly and resume its normal position. It is necessary to be sure that the liquid under treatment thoroughly wets the manometer. It may be useful to recapitulate the factors which contribute to securing correct boiling points. They are: (1) a dephlegmating column between flask and thermometer to remove superheated vapors; (2) a cavity or expansion in the column where the thermometer bulb is situated; (3) a limited opening between the thermometer cavity and the condenser; (4) a manometer situated on the side of the thermometer cavity and operated by the condensate; (5) a sensitive external manometer.

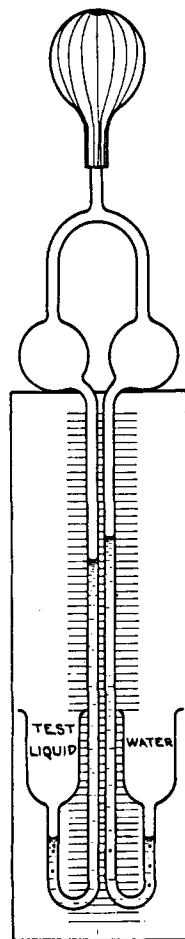


Fig. 13.

Summary

It has been shown that the usual distillation apparatus does not give true boiling points at low pressures.

Apparatus has been described which enables true boiling points to be secured.

A number of distillation experiments under vacuum have been described. A system of nomenclature for high boiling liquids has been suggested.

APPENDIX

A DIRECT READING OIL MANOMETER

Referring to Fig. 3, a simple U-tube is protected with splash bulbs at either end and is connected on the left-hand measuring side through a well-ground stopcock to the vacuum line. The other limb, in which a comparatively perfect reference vacuum is to be maintained, is connected with a miniature butyl phthalate condensation pump. The jets of this pump are only three or four millimeters in diameter and are surrounded by a cooling jacket communicating with a relatively large bulb painted black and situated above the main structure. The jacket is just completely filled with alcohol, the bulb is evacuated of all but the saturated vapor above the liquid and is then sealed off in the blow pipe flame. Hot vapors condensing at the jet cause the alcohol to boil at slightly above room temperature and send vapors into the flask, where they condense and return as liquid. The large surface of the bulb then becomes available for radiating the heat passing through the small surface of the pump. The jets are supplied with phthalate vapor through an electrically warmed and lagged tube from a boiling bulb some distance below. The condensate with entrained gases falls down a narrow tube having a preliminary dropping device which forms a secondary Sprengel backing pump. The gases are discharged into a storage bulb which connects by way of a second stopcock with the vacuum line. On commencing to use the manometer, the entrance tube is fastened to the pump, both stopcocks are opened, and the liquid in manometer and boiling bulb are thoroughly degassed. Presently, the condensation pump starts operating and the column in the reference limb rises a little, indicating that a good vacuum has been secured. The alcohol boils merrily into the black radiator bulb. The stopcocks are now closed, and the gage transferred to its place of operation. The left-hand stopcock is opened and the gage becomes available for readings. It is always shut off under vacuum. The reference side storage bulb should be re-evacuated every few days of continued use.

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