# THE PURIFICATION, PROPERTIES, AND USES OF CERTAIN HIGH-BOILING ORGANIC LIQUIDS\*

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Much laboratory technic has been made possible by the unique properties of mercury. A heavy, unreactive liquid of low vapor pressure and viscosity, it has proved eminently fitted for use in manometers, pumps, and gasometers where it provides an excellent liquid seal. It may well be called the universal fluid piston. Mercury has, however, some minor disadvantages which occasionally prevent its use. The objections will not always be of moment, but they are prohibitive in special cases. The properties of mercury which are of importance in the present paper are summarized in Table I.

## TABLE I

No.	Property	Remarks
Ι.	Mercury is metallic	The manometer column may be required not to conduct electricity. The metallic vapor may be objectionable.
2.	Mercury has a very high surface tension.	Does not form a definitely reproducible meniscus. The column may stick in glass tubes.
3.	The vapor pressure is above 0.001 mm. at room temperature.	A powerful refrigerant must be used for high-vacuum work.
4.	Mercury vapor is monatomic.	The vapor is not so easily condensed as is that of associated liquids.
5.	Mercury does not dis- solve foreign gases.	Mercury is immensely superior in this respect to all common fluids.
6.	Mercury is an element.	Mercury will withstand boiling indefinitely with- out alteration, in which respect it is superior to all organic liquids.

It will be seen that there is a sphere of usefulness for liquids which are superior to mercury in one or more of the first four particulars. There is also a field for a liquid which will lubricate the mercury meniscus, allowing it to slip without static friction along glass tubes. The present research was under-

<sup>\*</sup> Communication No. 394 from the Kodak Research Laboratories.

taken primarily to find a fluid to lubricate the meniscus of a mercury column in a special apparatus which has been described elsewhere.<sup>1</sup> It was found that a survey of many collateral and dependent matters was involved; and this paper is an account of such of these as may prove of general interest.

The most important characteristic of a liquid to replace mercury is low vapor pressure. Second in importance is stability on boiling. In this connection we must be able to secure the liquid in a pure state and should be able to ascertain the relation between the pressure of its vapor and the temperature. The distillation of high-boiling organic liquids is therefore a necessary preliminary to the study of the liquids themselves. The special apparatus which we have evolved for these distillations have been described in preliminary notices appearing in the Journal of the American Optical Society,<sup>2</sup> and in a technical circular.<sup>3</sup> We now offer a more comprehensive account.

Vacuum Distillation.—A substance of limited stability will generally approach decomposition as the temperature rises. If the boiling occurs at a low temperature, the substance becomes automatically protected from thermal damage. When boiling occurs normally at too high a temperature, it may be necessary to reduce the pressure so that the new boiling point may be below the limit of instability; we institute vacuum distillation. Whether the beneficial effect of evacuation on stability is due solely to the lower temperature of boiling or is assisted by the longer free path secured for the molecules in the vapor phase, is a moot point. We conceive however that both temperature and free path are of importance, although only the former can influence the internal translatory movement of the molecules.

We must distinguish at the outset most carefully between distillation and fractionation. Distillation may *achieve* fractionation when the boiling points of the mother liquid constituents are widely separated; but in other cases special precautions should be taken to prevent condensation of the lower boiling fraction while the higher boiling is being collected. In the remarks immediately following, we refer, except where otherwise specified, to distillation, and the condensation of all\* the components volatilized from the parent liquid.

Consider the conventional distilling flask and receiver pictured in Fig. 1. The liquid in the flask gives off vapor at its surface which passes towards the neck in the slow stream, A. At the neck, the molecules become crowded in the faster stream, B,\*\* whence they must again become accelerated on passing into the narrow tube, C. The mean forward molecular velocity in each section will be inversely proportional to the square of the diameter of the section. Thus, if the flask is 10 cm. in diameter and the vapor stream at A is moving upwards at 10 cm. per second, the velocity in B whose diameter is two centimeters must be 250 cm. per second. In the side tube, C, of diameter of half a centimeter the velocity is 40 meters a second.

 $<sup>\</sup>ast$  This does not include volatile impurities and products of cracking which may be removed by the pump.

<sup>\*\*</sup> We are considering pressures above 1 mm. of mercury where the mean free path is small. At very low pressures the forward molecular velocity remains unaltered.

Now the flow of gases through tubes at ordinary pressures is deducible from Poiseuille's equation<sup>4</sup>

$$\mathbf{q} = \frac{\pi \mathbf{D}^4}{128 \ \eta \mathbf{L}} \cdot \mathbf{p} \left( \mathbf{p}_2 - \mathbf{p}_1 \right)$$

The quantity of gas transferred is dependent on the product of the pressure and the pressure difference which in this case is approximately equal to the square of the pressure in the flask. The quantity is also dependent on the fourth power of the diameter of the tube and the viscosity of the gas.



Fig. 1

Now q in the equation is the quantity p.v. of gas transferred from the flask measured in cubic centimeters and millimeters of mercury, hence

$$p.v. = \frac{\pi D^4}{128 \eta L} \cdot p^2$$
  
and  $p = \frac{v.128 \eta L}{\pi D^4} dynes per cm^2$ 

In our original postulate v is 780 c.c. per second, L is 20 centimeters, while  $\eta$  may be taken as 1.7 imes 10<sup>-4</sup>

whence P = 
$$\frac{780 \times 128 \times 1.7 \times 10^{-4} \times 20 \times 75^{\circ}}{(0.5) 4 \times 10^{6}} = 4.07 \text{ mm.}$$

We see, therefore, that a fall of pressure of 4.07 mm. is involved in the passage of the gas down the tube, and that even with a good vacuum secured at the exhaust end a pressure of at least\* 4 mm. must be produced in the flask to overcome friction in the exit pipe. There are many liquids which are unstable, however, even if volatilized at pressures as low as 0.001 mm. Now at pressures of the order of one bar and less, the laws governing gaseous flow alter entirely and may be expressed according to Knudsen<sup>5</sup> by

$$q = \frac{(p_2 - p_1)}{W\sqrt{\rho}}$$

<sup>\*</sup> The calculations given above do not account for the acceleration of the gas en masse from zero to a velocity of 40 meters per second.

where w is the frictional resistance of the tube and  $\rho$  is the density. For long circular tubes the flow becomes

$$q = 3809 \sqrt{T/M} \cdot D^3/L (p_2 - p_1)$$

Here the quantity increases with the cube of the diameter but inversely as the



first power of the length. This means that although narrow tubes do not offer quite such a great proportionate resistance at low pressures the mass of gas transferred becomes very small indeed.

A sample of fluid which in a certain distillation train distilled X cubic centimeters in half a minute at 10 mm. pressure, would take

about 1 hour at 1 mm. pressure, or 1 week at 0.1 mm. pressure, or 2 years at .01 mm. pressure,

and perhaps 40 years at .001 mm. pressure, and no added efficiency in pumping would accelerate matters.

The remedy, therefore, and the only remedy, if distillation is to take place at very small pressures in a reasonable time, is to redesign the apparatus,



making the diameter (D) large and the distance (L) between the distilling and receiving surfaces small. This can be done most simply by enclosing the liquid in a squat inverted U-tube. One end is warmed and the other kept cold and the vapor passes in the direction shown by the arrows in Fig. 2. Actually, if the vapor is to survive until the proper place, the whole region embraced by the angle has to be kept warm, a matter difficult of practical accomplishment. A 5° fall in the jacket temperature below that of the liquid may cut the distillation to one-half, and a substantial increase may produce decomposition of the vapor. We have therefore found it convenient to substitute for the U-vessel an alembic such as that pictured in Fig. 3.\* Here the retort passes directly to an inverted condenser of umbrella-like

form terminating in a drainage annulus and receiving flask. Vapor escaping from the surface in A can pass directly to B suffering no hindrance from the

<sup>\*</sup> The figure shows a still, more complicated than suggested in the text. For the use of these features reference should be made to the previous papers: J. Opt. Soc. America, loc. cit.

walls of the vessel. Such an alembic serves excellently for liquids of moderate volatility but the modification in design has still not been carried far enough for viscous mixtures with a very high boiling or non-volatile constituent. The failure to function is due partly to absence of ebullition or stir-



Fig. 4

ring, and a skin may form on the surface as the liquid recedes in A, which permits scarcely any vapor to reach B. Working from a 500 c.c. flask in the place of tubing, however, we found it possible to make an alembic of smaller depth and much larger working surface like the one shown in Fig. 4 which

has an evaporative area of 50 sq. cm. and a condensing surface of about double that amount. The pressure tending to collapse the two halves at the annulus is over 200 lbs. under complete exhaustion, and it is not surprising if a weight equal to that of a heavy man, pressing on the  $4\frac{1}{2}$ -inch alembic more often than not produces collapse. The point of weakness is the annulus: the convex top and bottom withstand the strain successfully. The



problem of catching the distillate without an annulus has yielded the apparatus of Fig. 5, where drops collecting at the point, P, on the condensing surface, B, fall down the tube, C, and out of the still.

There remains a practical difficulty to be removed. Langmuir<sup>6</sup> has shown that a surface wetted by a liquid condenses every molecule incident. If the liquid is substantially non-volatile at the temperature of the surface, the molecules will seldom re-evaporate and the surface will permanently remove all molecules that strike it. The walls act therefore as though they offered no barrier between the surface of the liquid and an indefinitely large evacuated vessel into which the vapor might pass and be lost. If, also, we imagine the tube, C, connected with a pump of great capacity, molecules of vapor entering will also disappear at a rate depending on the area of the opening and the resistance of the tube. Let the area of the opening be a and the effective area a'. Let also the superficial condensing area of the still be A and the effective area, allowing for re-evaporation, *etc.*, be A'. Now evidently a' and A' need be only slightly smaller than a and A, so that for comparison of a' with A' we may compare a with A. As a practical example, a flask in our possession has the following measurements: diameter of container 10 cm.; diameter of fall tube 1.5 cm. Neglecting the walls of the still, which may be kept warm by lagging, the ratio of A' to a', at a conservative estimate is  $10^2$ :  $1.5^2$  or forty-four and one-half to one. This means that if the substance we are distilling cracks, yielding one part in forty-four of non-condensable vapor, which can only be removed by way of C, then of every two molecules of gas in the alembic one will be condensable and one will not. Let us further suppose that the exit tube C is connected to an oil pump by tubing 5 mm. in diameter\* and 20 cm. long. The ratio now becomes A': a': :400:1. If the pressure is less than I bar, \*\* the gas is obeying molecular flow laws,<sup>7</sup> dependent on the cube of the diameter, and the ratio of A' : a' will be vastly greater than A : a and will be in excess of 10<sup>3</sup>:05<sup>3</sup> or eight thousand to one. A decomposition of 1% or an evaporation of 1% of residual solvent or some more volatile impurity will maintain in the alembic anywhere from 8 to 80 molecules of something other than the distillate for every molecule of the latter.

The effect of the gaseous impurity is to decrease the mean free path of the molecules, which in turn reduces the likelihood of a vapor molecule reaching the condenser. The inert gas blankets the evaporative surface just as argon prevents volatilization of tungsten from a metal filament in a gas-filled lamp.

It has been deduced from the kinetic theory<sup>s</sup> that the mean free path is inversely proportional to the density, and therefore varies almost directly with the pressure. It is affected also by the viscosity of the gas, the molecular weight and molecular projective areas, and the temperature. It is therefore not possible to predict the exact free path of the particular substance which the reader may choose to distill. On the other hand, it is possible to predict the average free path of the oxygen and nitrogen molecules remaining at any given residual pressure from the equation:<sup>sa</sup>

## $\eta$ = .3502 p.14551 $\sqrt{T/M} \cdot L$

when  $\eta$  is the internal viscosity,  $\rho$  the density, and L the mean free path.

With air the average path is 8.6  $\sqrt{T/273} \times 10^{-6}$  cm. at atmospheric pressure.

At 1.0 mm. of mercury the average free path is	0.00562 cm.
o.1 mm.	.0562
.01 mm.	. 562
.001 mm.	5.62

The table shows that unless the pressure of the residual gas is less than one thousandth of a millimeter of mercury, the average path of the vapor molecules will not be sufficient for the majority to reach the condensing surface without collision. Fairly volatile liquids which we may distill at above o.t

<sup>\*</sup> This is an unusually large diameter for most thick-walled tubing.

<sup>\*\*</sup> One millionth of an atmosphere.

mm. carry forward the residual gas and push it into the exit pipe so that it is rapidly brought to an unmeasurable concentration—the still acts as its own condensation pump. The vapor then streams towards the condensing surface, with many collisions it is true, but without the forward product of the collision being most often an uncondensable molecule. Distillation and condensation are thus extremely rapid.

It is when the vapor pressure of the distillate is of the same order as the pressure of the residual gas that this residuum must be so perfectly removed. The harmful pressure is a direct function of the average free path. If the distance between the distillation and condensation surfaces is  $5 \text{ cm}_{...}$  the pressure must be less than 0.001 mm.; if 0.5 cm., then less than 0.01. We have accordingly constructed some distilling vessels in which the surfaces have been brought very close indeed without impairing the facilities for

removing the residual gas. In the three figures (Figs. 6, 7, and 8) shown, A is the exit pipe to the pump,  $\sum$ B the outflow tube(s) for distillate, C the condensing surface, and T a recess for the thermometer. The type of vessel which is chosen is purely a matter

A F1G. 6

of expediency. No 6 must be small to avoid constructional weakness and will be useful for samples up to 50 c.c. Its advantage is an under surface free from protrusions, enabling the still to rest on a hotplate.\*

The type shown in Fig. 8 can accommodate 200 c.c. of liquid which it will then distill into three portions without breaking the vacuum. It is so clamped that it can be tilted about the axis of the exit tube, A. The receiving flasks are fastened by well-matured rubber stoppers to the tubes, B. The liquid is

introduced through the constricted tube, E, which is then sealed, and the vessel is tilted to a somewhat acute angle. Evacuation is commenced and then gentle heating is applied until frothing ceases and distillation starts. The first runnings and splashings fall from the tip, P, against the wall of the fall tube, and wander into  $B^2$ . The flask is now tilted again for the distillate to drop into the

FIG. 7

funnel communicating with  $B^1$  until a sufficient fraction has been collected. Another shift of position enables a further fraction to be caught in  $B^3$  while the residue remains in the still.

The collection of three fractions in series is an advantage possible only when the vapor pressures of the first fractions in the cold flasks is lower than the vapor pressure of the hot mother liquid in the still. This may not be the case and it may be necessary to remove the involatile material. This can be done virtually by placing solid carbon dioxide around  $B^1$  and  $B^2$  but it is more satisfactory to disconnect and empty the flasks. The whole advantage of the triple catchment device then becomes superfluous and we



<sup>\*</sup> The heat input required by these stills is so small and needs such careful adjustment that the ordinary hotplate is not so convenient as the special coils used by the other stills.

may use a vessel of the kind shown in Fig. 7. The innovation here is that the floor and ceiling are protected from "implosion" by the strut, D. We have made, from ordinary Pyrex flasks, vessels of this type which will hold 500 c.c. in the distilling portion. The distillate collecting on the roof runs down the strut and emerges at B into a flask. When it is desired to pass from one fraction to the next the vacuum is relieved and the flask changed.

When every precaution has been observed to secure the highest vacuum, the rate of distillation remains limited by the rate at which molecules leave the liquid surface at the temperatures in question. This rate, according to Langmuir<sup>9</sup> must be equal to the rate of condensation from a saturated vapor at the same temperature. It is deducible from the expression:

W =  $4.374 \times 10^{-5} \times 60$ . P $\sqrt{M/T}$ 

where W is the weight in grams of substance of molecular weight, M condensing each minute per square centimeter at a pressure of P bars at an



F1G. 8

absolute temperature, T. The rate at 100°C. for a substance of molecular weight of 200 can be shown to be 25 p grams per minute, where p is the pressure in millimeters of mercury. Thus, an alembic of 10 cm. diameter should yield distillate at a maximum rate of  $\frac{5.^2 \pi \cdot 25}{1000} = 1.96$  grams per minute,

at a pressure of 0.001 mm. This agrees fairly well with the best results obtained in practice.

The relation holds good only for pressures so small that the evaporation is not sufficiently rapid to cool the surface of the liquid. Above one millimeter the deciding factor must be the rate at which heat can be passed into and through the liquid without local over-heating; and the rate at which it can be removed from the condensing surface.

This brings us to the question of securing and maintaining a sufficient vacuum. We require a good backing pump which for example may be a "Hyvac" or "Megavac" or equivalent. In conjunction with this is needed a condensation pump and at least two suitable condensation traps; lastly some matured rubber stoppers and some thick-walled, large-diameter rubber tubing. A complete assemblage is shown in Fig. 9. The distilling flask with heater, thermometer, and receiver is supported at A and is joined to the trap, B, by a stout rubber tube, C. The large internal tube of the trap is joined to the condensation pump. The small external pipe from B passes to the McLeod gauge and a U-tube manometer. The line may well be protected by an automatic shut-off valve such as that recently described elsewhere.<sup>1</sup> The high pressure side of the condensation pump is joined to a second refrigeration trap, G, whence the line passes to the oil pump. It is useful to place a by-pass tube, E, between the far side of the trap and the high vacuum side of the condensation pump, and to place in the bend a few drops of butyl phthlate. A slight displacement of the levels shows that the pump, which may be operated by butyl phthalate instead of mercury, is working. Finally it is convenient to include two well-greased three-way stopcocks, F, just before



F1G. 9

the oil pump so that preliminary volatiles may be deflected into a flask cooled with ice and salt. This may be omitted if the liquid is prepared elsewhere for distillation, or if the pump is "blown out" regularly.

We will now discuss the units of this equipment.

The Rubber Seals.—For the most exacting work all connections may be made by fusing the glass. With practice, however, this becomes unnecessary, since matured rubber acquires a vapor pressure less than most liquids under distillation. The rubber need never be exposed in long lengths. Stout red rubber tubing containing little sulfur (as supplied, for instance, by the Central Scientific Instrument Company) is cut into convenient lengths and placed in a flask and it is evacuated over night while the flask reposes in the 80°C. oven. After this maturing treatment, the rubber is pushed  $1\frac{1}{2}$  inches to 2 inches over each end of glass, the ends of which are made to touch. Castor oil is rubbed over the rubber especially at the ends and is wiped off after the experiment. The same treatment and precautions apply to the rubber stoppers. Rubber prepared in this manner is ready for use at any time and should not require reheating.

The Vapor Traps.—It must be emphasized that the condensation pump cannot work at its full efficiency unless the lead-in tube on the high-vacuum side is at least as wide bore as the pump itself.<sup>4</sup> Alternatively if the size of

the tubing is limited by other considerations, a quite miniature pump can be used.\* We recommend a bore of about 2 cm. which demands that the trap, B, shall be of wide diameter. To prevent choking the entrance to the trap should always be by the side arm, which is kept well above the level of refrigerant. The lead tubes of trap, G, may be smaller because the pressure here is higher. Refrigerant should never be placed in all the traps at the beginning of distillation. The flask, H, should be surrounded first with ice and salt, and should be shut out of the pipe line when vapor ceases to condense. Trap, G, may now be packed with solid carbon dioxide and the distilling vessel watched for signs of sublimation. The trap, B, should never be cooled unless the pressure given by the McLeod gauge is less than 0.01 mm. Below this pressure it is well to freeze out butyl phthlate and other vapors so that the mean free path in the still may become large. If the refrigerant is applied at this place too early, volatiles may be condensed at a high pressure which will evaporate later at a low pressure, in spite of the reduction in temperature, and it may take hours or even days to rid the apparatus of contamination.

The McLeod Gauge.—The McLeod gauge will often be contaminated with condensable vapors and will not give a true reading of pressure in the pipe lines or particularly in the hot still. It will, however, give a fairly accurate indication of the residual gas and this, as we have shown, is often the critical factor.

Temperature Control.—It has been found quite untrustworthy to express the boiling points of liquids in these stills as a function of the pressure at which they begin to sublime. The thermometer is useful merely to follow the progress of heating. In general, the vapor pressure doubles for every rise of from 6°C. to 10°C. The evolution of decomposition products on the other hand may increase a hundred-fold for a similar rise in a critical temperature region. The decomposition products hinder distillation and we have often encountered the paradox that sublimation increases as the temperature is lowered. The temperature of distillation should be noted carefully as a guide to future work but no conclusion as to the boiling point: pressure relation should be drawn.

Breaking the Vacuum.—Dissolved gases and volatile solvents prevent a sufficient vacuum for distillation being obtained for so long a time on first treating the liquid that the operator might be loath to admit air for changing the receivers. Actually it is found that distillation is resumed rapidly after reevacuation because only a negligible quantity of air dissolves in the hot liquid during the few minutes of interruption.

Preparing the Liquid.—Much frothing and preliminary heating may be avoided in the still if the liquid is treated first for the removal of solvents. Air or nitrogen may be blown through for a couple of hours while the liquid is held in a flask warmed in a basin of water. The warmed liquid may equally well be treated by suction from an ordinary filter pump.

<sup>\*</sup> See later for description of miniature pump.

Blowing out the Oil Pump.—The oil pump draws in volatile solvent and air on the suction stroke and condenses the solvent portion in the oil during compression. The oil may of course be rectified by distillation, but it may often more simply be "blown out." A rubber tube is so clipped on the intake that air is sucked in sufficiently to discharge bubbles of about 10 c.c. in volume under the oil. The pump is run all night in this manner and thereby subjected to about maximum load. The oil becomes quite hot and the solvent is blown off. In the morning the pump is run with the tube completely closed and becomes ready for use in about an hour.

Preparing a High-Grade Pump Oil.—There seems no mechanical reason why an oil pump should not exhaust to less than 0.001 mm. of mercury if the oil has a vapor pressure less than this amount. The best commercial pump oils measured after continued refluxing in our tensimeter indicated a vapor pressure of about  $10^{-6}$  mm. at room temperature. The apparent vapor pressure of the pump oil is due to the products of cracking which are always present from the distillation during manufacture. They confer, in fact, a definite smell. Redistillation under vacuum in an ordinary distilling flask is no remedy, for it generates as many products as it removes. When, however, the oil is fractionated in a sublimation still, a middle portion of golden yellow color is obtained entirely free from odor which exhibits no readily measurable vapor pressure at ordinary temperature. The material is recommended for pump fillings when a condensation unit is not available. We have not yet had an opportunity of determining the lower limit attainable with the refined oil.

Perhaps the best guide to using a sublimation still will be furnished by an extract from our notes covering an actual distillation. Tri-benzyl citrate was prepared by condensing citric acid and benzyl alcohol with some hydrochloric acid in the presence of much xylene. The water from the reaction was separated and the benzyl alcohol mostly removed by pre-treatment under vacuum. After cooling, the resulting crude white mass was remelted and 200 c.c. introduced into the still. It was then warmed to 50°C, while much air was thrown off. Distillation commenced and 50 c.c. of a straw-colored fluid collected after which the transfer stopped and showed no tendency to continue during two hours. The receiver was then emptied of distillate, which proved to be benzyl alcohol, and was replaced by a clean one. The temperature was raised to 110°C. and pumping continued for twelve hours but no distillation took place. The temperature was therefore lowered to 86°C, and the high-pressure trap (G) was cooled. No sublimation occurred for a further eight hours, when suddenly the material began to come over rapidly. In an hour or so 90% had passed into the receiver where it eventually set to a white crystalline solid. The McLeod gauge registered no difference in pressure between the periods just before and during final distillation. showing that the inhibiting impurity was condensable at atmospheric pressure. We have not found any reference in the literature to the distillation of tribenzyl citrate.

### The Uses of High-Boiling Organic Liquids

We have distilled a number of materials in the above manner and have determined their vapor pressures,<sup>10</sup> surface tensions, their capacity for dissolving air,\* and their effect on the mercury meniscus.<sup>11</sup> About this time there appeared in Nature<sup>12</sup> a note by C. R. Burch on the use of heavy hydrocarbon oils to replace mercury in the Langmuir condensation pump. Dr. C. E. K. Mees suggested that we try the liquids, about which we had now collected so much data, in the hope that some might show an advantage over mercury.

N-di-butyl phthalate, from other evidence, seemed the most likely fluid and was accordingly tried; with success. Butyl phthalate has a vapor pressure one hundred times less than mercury at room temperature and the di-



vergence increases as the temperature falls. We were able to build miniature air-cooled pumps which would utilize the phthalate\*\* and run them in conjunction with the Hyvac oil pump. This pump and others are being detailed, with charts of their performance, elsewhere,<sup>13</sup> but a useful laboratory pattern may be described here. The butyl phthalate gives the same maximum speed of exhaust as mercury, but is more sensitive to wattage input and requires a slightly lower backing pressure. The great advantage is its low vapor pressure and the elimination of mercury vapor, enabling a trap to be omitted for most chemical operations. The pump is extremely simple. A glass tube, 15 mm. internal diameter, is blown into two bulbs as shown in Fig. 10. The upper bulb is pushed in to yield an alembic, taking care that the jet is about 7

<sup>\*</sup> See page 652.

<sup>\*\*</sup> Mercury works equally well in the miniature pump.

mm. away from the receiver. The annulus is connected to the lower bulb by a slender trapped pipe. Stout copper wire twisted into spiral loops at frequent intervals is wrapped around the stem in close formation. The loops are so hammered that the points of departure are not thicker than the parent wire. The copper is then blackened with dilute ammonium sulfide. A heater absorbing some thirty or forty watts at seventy volts is then wound on an asbestos horseshoe and packed against the bottom. Thirty cubic centimeters of butyl phthalate is poured in and the pump run in vacuo with the heater connected with an adjustable resistance to the 110-v. mains. When the best wattage input is determined, a small resistance is wound equal to that of the adjustable resistance for which it is substituted in series with the heater. A switch is provided to short circuit the subsidiary resistance during the warming up period.

These little condensation pumps are so light and convenient that they may be included as boosters in all manner of vacuum apparatus. They may be suspended in the glassware train without special support. Cooling may be assisted by a long paper chimney or by a fan. The best wattage input varies with the cooling. With no forced draft, a small input gives as good a speed of exhaust as a larger input with a well-cooled pump. The only advantage of the greater cooling is that exhaustion commences at a higher backing pressure. We use uncooled pumps in most of our own work. Besides di-butyl phthalate we have tried:

di-benzyl phthalate	ethyl oleate
butyl benzyl phthalate	"Nujol"
n-amyl phthalate	vacuum pump oil
iso-amyl phthalate	tri-cresyl phosphate
butyl stearate	di-benzyl malonate etc., etc.
methyl oleate	monochlophthalane, etc.

Butyl benzyl phthalate is the only member equal to butyl phthalate in speed and reliability. It has a lower vapor pressure but is much more expensive. All the other materials are slower or of no use at all. The superiority of the butyl phthalate is evidently due to its stability. A sample was sealed in a small electrically warmed tube under torricellian vacuum (Fig. 11). and the fall of the pendent mercury column plotted with time. The phthalate refluxed gently at  $130^{\circ}$ C., maintaining vapor halfway up to the tube. A little gas was given off during the first day and was withdrawn, resealing the apparatus. Thereafter the pressure rose at about a millimeter a week, the rate increasing as the temperature of distillation was raised.

If the products of decomposition had a molecular weight equal to carbon dioxide, this would give, for the sample used and under these vacuum conditions, a half period of decomposition of 36,000 years; supposing always that no change took place in the liquid phase. When the phthalate was boiled in a tube containing a piece of brightly polished steel, no decomposition occurred for 24 hours but later the liquid became dark gray. Phthalic anhydride sublimed on the upper parts of the tube and quantities of gas were evolved. The phthalate is not suitable for use in metal pumps. The other liquids listed continually evolved minute quantities of gas on boiling. Benzyl butyl phthalate and iso amyl phthalate could be boiled for a day without appreciably relieving the vacuum, but the stearates, oleates, and malonates, and the higher paraffins, all showed continued decomposition. Evidently these bodies fail to give good pumping action because they are burdened with the task of blowing off their own waste products. The highboiling paraffin hydrocarbons consist of many isomers. It is possible that some of these are less stable than others, and may be eliminated with long boiling. We tried the straw-colored fraction from the sublimation of vacuum pump oil and found a very poor efficiency in the condensation pump. After two days' use, however, it exhausted as well as butyl phthalate. It did not attack iron and could be used in a metal pump. On the other hand, it charred more readily than the phthalate and would consequently entail more frequent cleaning of a pump than mercury. The following summary may prove useful:

Fluid used		Vapor Pressure at	
in Pump	Behavior	25°C.	o°C
Mercury		$_{2.3} \times 10^{-3}$	$2.4 \times 10^{-4}$
Butyl phthalate	Attains maximum efficiency a few minutes after commencement of boiling.	7.8 × 10 <sup>−5</sup>	3.5 × 10 <sup>-6</sup>
Butyl benzyl phthalate	Requires boiling for some hours initially. Works well in few min- utes in subse- quent operations.	6.2 × 10 <sup>−6</sup>	2.6 × 10 <sup>-7</sup>
Heavy hydro- carbon	Requires two days initial boiling. Chars on continued use.	2.9 <b>-</b> 4.0 × 10 <sup>-6</sup>	1.2 <b>-</b> 2.1 × 10 <sup>-7</sup>

Lubricants for the Mercury Meniscus.—When a drop of mercury is splashed on glass it breaks into minute drops which, in spite of their great comparative weight, fail to move when the glass is tilted. Both clean and dirty mercury stick to glass. The adhesion is in evidence although less pronouncedly when mercury moves in a glass tube. The meniscus flattens as the mercury ebbs and bulges as it flows. The angle of contact and the actual height of the crown vary for a given head with the last direction of movement and with the nature of the surface film. It would be a distinct advantage for physical measurements, and for many mechanical devices, if the mercury could be made to wet glass and thus assure a contact angle of zero—or else could be so perfectly insulated from the glass that it maintained an angle of 180°. We have found that within limitations the latter condition can be secured. Very clean mercury in vacuo sticks to glass because of the intrinsic attraction of mercury and glass. The surface of the mercury, since it has no film other than that of the boundary mercury atoms, which exhibit temporarily the special properties conferred by their position, is interchangeable with the bulk of the liquid. Work done in pulling the mercury away from the glass on one side of the globule should be returned by the approach of other portions on the other side. When there is a layer of oxide, whether one or many molecules thick, the layer is not interchangeable with the liquid bulk, and movement must rupture the layer. This is the usual practical condition. Mercury in a glass tube must be considered "sheathed over" the meniscus and far down the cylindrical portion adjacent to the glass walls with a layer

of oxide. On receding this layer must be ruptured and crumpled against the force of surface tension. A supernatant layer of organic liquid facilitates the passage of mercury in at least three ways. It may assist the crumpling of the film; it may insulate the film from the glass and allow it to move without crumpling; and it may dissolve the film altogether. Almost any true lubricant<sup>14</sup> will perform the first function. For the second it is necessary to add to the fluid a substance which is adsorbed so heavily to the glass that the film does not adhere. Mercury di-p-tolyl in butyl phthalate, or mercurous nitrate in water are both effective. Complete solution of the film may be secured by free halogen in a suitable solvent; by powerful reducing agents; and by the mercaptans and allied sulfur bodies.<sup>15</sup> No mercaptan has



been found which does not ultimately yield a second film of mercury sulfide, but the film appears excellently lubricated against the glass.

A lubricant for mercury in high-vacuum apparatus must have a negligible vapor pressure.

For the most exacting requirements where low pressure is more important than perfect lubrication we recommend di-benzyl phthalate saturated with mercury di-p-tolyl. When the exhaustion is continually performed, the same solvent, or di-butyl phthalate, containing 1-5% phenyl hydrazine (base, not hydrochloride), gives quite perfect lubrication. A little nitrogen is evolved and perhaps some benzene and water, but in such small amounts that they pass unnoticed to the pump. For experiments lasting a day only butyl phthalate or higher boiling solvent containing one per cent of thioacetanilide may be used. Any of these fluids allowed to float to a depth of a millimeter, above the column in a mercury barometer will allow the meniscus to move without sticking or without changing shape. Readings with the cathetometer may be made with extreme accuracy. The fluids all have the disadvantage, not shared by mercury, that they dissolve air and other gases. The solubility by volume of air at  $20^{\circ}$ C. is given in the accompanying table.

Substance	Solubility
Ethylene glycol	4.7%
Tri-o-cresyl phosphate	5.4
Alpha chlor naphthalene	7.2
Alpha chlor naphthalene (crude)	12.0
Triacetin	9.4
"Nujol"	10.1
Ethyl ether of ethylene glycol	11.7
Methyl oleate	12.4
Ethyl oleate	14.0
Butyl stearate	18.1
Iso-amyl phthalate	8.9
N-di-butyl phthalate	9.0
Butyl benzyl phthalate	9.3
Butyl terephthalate	9.7
Methyl glycol phthalate	11.6

This solubility of gases renders the fluids unsuitable for use in gasometers, or manometer tubes, unless, in the latter case, precautions are taken to remove gases liberated in the high vacuum limb. A very delicate manometer sensitive to at least 1/100 mm. can be made from a two-stage condensation pump, using mercury and a U-tube filled with dyed phthalate (Fig. 12).

Both ends of the manometer tubes are open to the source of pressure change and sudden admission of air causes no harmful return of the liquid column. When the manometer is connected to the vacuum line this line acts as the backing pump of the two-stage mercury pump. A substantially perfect vacuum is produced in one limb while the pressure to be measured depresses the liquid in the other. Gases dissolved in the phthalate column are removed immediately as they leave either meniscus.

#### Summary

The replacement of mercury by high-boiling organic liquids in certain physical operations is described.

A method of procedure for high vacuum distillations is outlined.

A condensation pump operating from organic liquids is described.

An explanation is advanced for the adhesion and sticking of mercury in glass tubes, and a series of lubricants are named which prevent the adhesion.

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<sup>5</sup> Ann. Physik, 28, 76 (1909).

<sup>6</sup> Phys. Rev., 8, 149 (1916); Knudsen: Ann. Physik, 47, 697 (1915).
 <sup>7</sup> See Dushman: "High Vacuum," General Electric Review Press p. 30, et seq. (1922).

<sup>8</sup> Dushman: loc. cit. p. 13.

<sup>a</sup> Dushman: loc. cit. p. 13.
 <sup>a</sup> Phys. Review, 2, 329 (1913).
 <sup>a</sup> A Low-Pressure Tensimeter. J. Phys. Chem., 34, 627 (1930).

<sup>11</sup> J. Opt.Soc. America, **19**, 190 (1929).

<sup>10</sup> Notice, America, 19, 190 (1929). <sup>12</sup> Nature, Nov. 10, p. 729 (1928). Since assembling this article a paper by C. R. Burch has appeared (Proc. Roy. Soc., **123A**, 271 (1929), covering substantially the same subject material. The practical methods of the present writer differ considerably from those of Burch and the present contribution is offered without further apology.

<sup>13</sup> Rev. Sci. Instruments, 1, 140, March (1930). <sup>14</sup> See Hardy and Doubleday, Proc. Roy. Soc. 100A, 500 (1921): 101A, 489 (1922); 104A, 25 (1923); 108A, 1 (1925).

<sup>15</sup> Suggested to the authors by Dr. S. E. Sheppard of this laboratory.