MOLECULAR DISTILLATION AND SUBLIMATION.

By P. C. CARMAN.

In comparatively recent years, the process of molecular distillation has been developed to the status of a large-scale, chemical engineering unit operation ; but there has been little discussion of its general limitations, or of its relationship to other modes of distillation. Articles on molecular distillation leave the general impression that it becomes operative only at pressures of the order of 10^{-4} mm. and that the distance of the condensing surface from the evaporating surface must be less than one mean free path of the vapour molecules.[1,2] It is proposed to show here that molecular distillation has a much wider scope than would be suggested by these limitations.

Distillation implies a combination of the following stages : (i) transfer of heat to an evaporating liquid to provide latent heat of vaporisation and to maintain the liquid at absolute temperature, T, (ii) formation of vapour at the liquid-vapour interface, (iii) transfer of vapour and (iv) condensation of vapour at a condenser surface maintained at a relatively low temperature, T_c. In text-books on distillation, little attention is devoted to the fact that formation and transfer of vapour is achieved by three distinct mechanisms, which may be described as (a) ebullition, (b) normal evaporative distillation and (c) molecular evaporative distillation or molecular distillation. The relationship between these can be explained by considering a liquid maintained at constant temperature, while the pressure, P, in the space above it is gradually decreased. Initially, P is much greater than the saturation vapour pressure, Π, of the liquid at temperature, T, so that an inert gas, such as air, is present, through which vapour produced at the liquid surface is transferred by diffusion and/or convection to the condensing surface. Under these conditions of *normal evaporative distillation*, the rate of distillation is controlled by the rate of mass transfer between evaporating and condensing surfaces, not by the rate of heat transfer. If the rate of heat transfer is increased, the liquid rises in temperature till the increase in Π produces a corresponding increase in rate of mass transfer.

If P is decreased till it is equal to Π, bubbles can form and grow in the liquid, so that distillation normally takes place by *ebullition*. The rate of distillation is here controlled by the rate of heat transfer, since the temperature of the liquid remains constant, while the liquid-vapour interface can be increased to an unlimited extent by formation of bubbles. Above the liquid, vapour is not transferred by diffusion or convection, but by bodily movement, and, as the condenser must usually be well separated from the boiling liquid to avoid splashing, there can be a distinct difference in total pressure between boiler and condenser, owing to frictional losses.

For most common liquids, there is thus an abrupt change in the mode of distillation when P is decreased to Π, and P cannot be decreased below Π. In the case of many oily liquids with very high boiling points, Π is very small up to the highest temperatures to which it is safe to heat them, and, under these conditions, bubbles do not form readily. It is then possible to decrease P below Π, and there is a more-or-less gradual change

[1] *J. Soc. Chem. Ind.*, 1939, **58**, 39 and 43.
[2] Hickman, *Chem. Rev.*, 1944, **34**, 51.

from normal evaporative distillation, controlled by rate of transfer of vapour, to *molecular distillation*, in which the rate of distillation is controlled by the absolute rate of evaporation, i.e. the rate at which molecules escape from the free surface of the liquid.

It is important to note here that *sublimation* of solids can be treated in exactly the same way as distillation of liquids ; and that, as ebullition is impossible, sublimation can only show the change from the normal evaporative to the molecular evaporative process as P is decreased.

Equations for Evaporative Distillation.

The transition from normal evaporative to molecular distillation or sublimation may now be discussed quantitatively. It is not easy to express rates of distillation quantitatively if convection is involved, but the essential points can be made clear by assuming that transfer of vapour takes place only by true diffusion to a parallel condenser, at a distance, x, from the evaporating surface and equal to it in area. Then, if

w = rate of distillation in g./cm.^{2} of liquid-vapour interface/sec.
M = molecular weight of vapour relative to $O = 16$.
D = coefficient of diffusion in cm.^{2}/sec.
P_i = partial pressure of vapour in dynes/cm.^{2} at liquid-vapour interface.
Π_e = saturation vapour pressure at T_e in dynes/cm.^{2}.
R = gas constant in c.g.s. units = $8 \cdot 3 \times 10^7$.

$$w = \frac{MDP}{RTx} \ln \left(\frac{P - \Pi_e}{P - P_i} \right). \qquad . \qquad . \qquad . \quad (1)$$

In this, DP is independent of P and proportional to $T^{3/2}$ so that

$$w = \frac{k}{x} \ln \left(\frac{P - \Pi_e}{P - P_i} \right) = \frac{k_1}{x} \log \left(\frac{P - \Pi_e}{P - P_i} \right) \qquad . \qquad . \quad (2)$$

where $k_1 = 2 \cdot 3 k = \dfrac{2 \cdot 3 MDP}{RT}$ and is proportional to $\sqrt{T}$, but is otherwise constant.

The usual practice in chemical engineering calculations is to assume equilibrium at the liquid-vapour interface, i.e. $P_i = \Pi$, whence

$$w = \frac{k_1}{x} \log \frac{P - \Pi_e}{P - \Pi} \qquad . \qquad . \qquad . \qquad . \quad (3)$$

and, if Π is small compared with P, this becomes

$$w = \frac{k}{x} \cdot \frac{\Pi - \Pi_e}{P}. \qquad . \qquad . \qquad . \qquad . \quad (4)$$

The equation generally employed for the absolute rate of evaporation, w_0, in molecular distillation is

$$w_0 = \Pi \sqrt{\frac{M}{2\pi RT}}. \qquad . \qquad . \qquad . \qquad . \quad (5)$$

Now, the right-hand side of this equation represents a calculation of the rate of collision of vapour molecules with the liquid surface in a saturated vapour. If no colliding molecules rebound, this equals the rate of condensation and hence the rate of evaporation, w_0. It follows that, if the partial vapour pressure at the liquid-vapour interface is P_i, the rate of collision and hence the rate of condensation will be $w_0 \cdot P_i/\Pi$, while the absolute rate of evaporation is unchanged. Then,

rate of distillation = absolute rate of evaporation — rate of condensation

or $$w = w_0 \left(1 - \frac{P_i}{\Pi} \right). \qquad . \qquad . \qquad . \qquad . \quad (6)$$

Eqn. (7) would still be obtained if the accommodation coefficient, α, is less than unity, i.e. if part of the colliding molecules rebound; provided that α is the same at vapour pressure, P_i, as at Π. In the following treatment, it will be assumed that this is true and that eqn. (6) is therefore valid. In the curves calculated for water in the next section, it is assumed that $\alpha = 1$, but they would be little affected if α had smaller values.

Putting (2) and (6) together,

$$w = w_0\left(1 - \frac{P_i}{\Pi}\right) = \frac{k_1}{x} \cdot \log\left(\frac{P - \Pi_c}{P - P_i}\right) \qquad . \qquad . \qquad (7)$$

emerge as the fundamental equations defining rates of evaporative distillation, i.e. by eliminating P_i, w can be calculated under any given set of conditions, P, x, T and T_c, the latter two quantities giving k_1, w_0, Π and Π_c.

Eqn. (7) lead to two important limiting approximations. First, solving for P_i in eqn. (6),

$$P_i = \Pi\left(1 - \frac{w}{w_0}\right) \qquad . \qquad . \qquad . \qquad . \qquad (6a)$$

whence, if w/w_0 is very small, $P_i \simeq \Pi$, i.e. eqn. (3) is obtained for normal evaporative distillation. As eqn. (3) only gives real values of w when $P > \Pi$, normal evaporative distillation is similarly limited.

Second, solving for P_i in eqn. (2)

$$P_i = P - (P - \Pi_c) \times 10^{-\frac{wx}{k_1}} \qquad . \qquad . \qquad (2a)$$

so that, when $\frac{wx}{k_1} > 1$, or $\frac{w}{w_0} > \frac{k_1}{w_0 x}$, the second term rapidly becomes very small, giving $P_i \simeq P$. It follows that the equation typifying molecular distillation is

$$w = w_0\left(1 - \frac{P}{\Pi}\right). \qquad . \qquad . \qquad . \qquad . \qquad (8)$$

This gives positive values of w only if $P < \Pi$. Clearly, over a more-or-less limited range of P near $P = \Pi$, a distillation is neither normal evaporative nor molecular, but a combination of the two as described by eqn. (7). Eqn. (2a) also apparently shows that P should be greater than P, if $P < \Pi_c$, so that molecular distillation is limited to $\Pi_c < P < \Pi$. The meaning of this is that, when $P = \Pi_c$, the vapour has this pressure at both the evaporating and the condensing surfaces, so that much of it is removed uncondensed by the vacuum pump. Actually, P can be reduced below Π_c, but the condenser then ceases to function, all vapour being removed by the pump, and the process ceases to be distillation.

Evaporative Distillation of Water.

Further discussion of eqn. (7) in terms of mathematical symbols would not be very fruitful, so that the essential points are illustrated by plotting curves for water. Rates are plotted as ratios, w/w_0, against the variable of chief interest, P, using logarithmic scales in both cases. Curves in Fig. 1 and 2 are for $20°$ c., $-20°$ c., $-50°$ c. and $-80°$ c. when $x = 1$ cm., and in Fig. 3 for $x = 1$ mm., 1 cm., and 1 m., respectively, when the temperature is $-20°$ c. It is assumed that the condenser temperature is always so low that Π_c can be neglected. Thus, eqn. (7) become

$$\frac{w}{w_0} = \left(1 - \frac{P_i}{\Pi}\right) = \frac{k_1}{w_0 x} \cdot \log\frac{P}{P - P_i} \qquad . \qquad . \qquad (7a)$$

and eqn. (3) becomes

$$\frac{w}{w_0} = \frac{k_1}{w_0 x} \cdot \log\frac{P}{P - \Pi} \qquad . \qquad . \qquad . \qquad (3a)$$
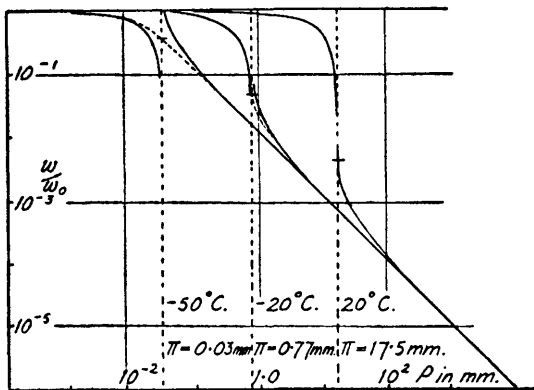
FIG. 1.—w/w_0 against P at three different temperatures, $x = 1$ cm.
Full curves for equations (3a) and (8), broken curves for equation (7a).

FIG. 2.—w/w_0 against P at $-80°$ C., $x = 1$ cm.
Full curves for equations (3a) and (8), broken curve for equation (9),
dotted curve for mean free path correction, equation (10).
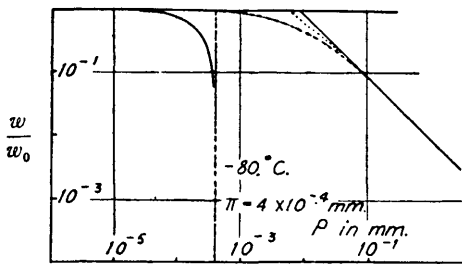

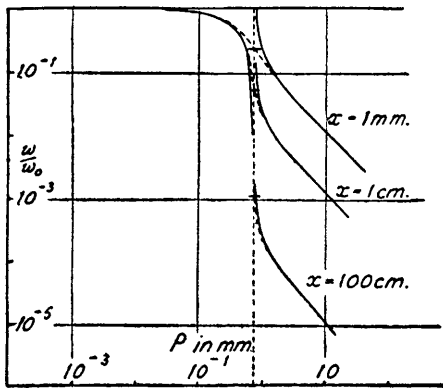FIG. 3.—w/w_0 against P at $-20°$ C. for three values of x.
Full curves for equations (3a) and (8), broken curves for equation (7a).

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Experimentally, for water vapour-air at $0°$ c. and 1 atm., D is $0·22$ cm.^{2}/sec., from which it can be calculated that

$$k_1 = 4 \times 10^{-4}, \text{ in consistent c.g.s. units.}$$

Other essential data are as follows :

Temperature.			Π in mm.	w_0.	w_0/k_1.
$20°$ c. (water)	.	.	$17·5$	$0·25$	600
$-20°$ c. (ice)	.	.	$0·77$	$1·2 \times 10^{-2}$	$30·4$
$-50°$ c. (ice)	.	.	$0·03$	$4·9 \times 10^{-4}$	$1·34$
$-80°$ c. (ice) .	.	.	4×10^{-4}	$7·1 \times 10^{-6}$	$2·1 \times 10^{-2}$

In Fig. 1-3, the true curves given by eqn. $7(a)$ are plotted as broken curves for each set of conditions, and it can be seen how these merge into the limiting eqn. $(3a)$ and (8) which are plotted as full curves. The value of w/w_0 for $P = \Pi$ is also clearly marked. The fact that the curve at $20°$ c. refers to liquid water and the others to ice is immaterial, since almost exactly the same curves will be given for liquid and solid, provided they are compared, not at the same temperature, but at the same values of Π and of x. The curves for ice at $-20°$ c. have recently become of great importance, since it is the temperature employed for removal of water from aqueous penicillin solutions.

First consider water at $20°$ c., this being characteristic also of higher vapour pressures. Even when P is decreased to Π, w/w_0 is extremely small, so that eqn. $(3a)$ for normal evaporative distillation applies with great accuracy down to $P = \Pi$, at which water boils. If, however, boiling could be prevented, or if ice could exist with the same vapour pressure, the curve in Fig. 1 shows an abrupt transition to molecular distillation as given by eqn. (8) when $P = \Pi$, accompanied by a great increase in rate of distillation.

The behaviour of ice at $-50°$ c. in Fig. 1 typifies evaporative distillation of substances with low vapour pressures. Here $w/w_0 = 0·35$, when $P = \Pi$, with the result that there is no sharp change from normal evaporative to molecular distillation, and there is a considerable range on either side of $P = \Pi$ for which eqn. $(3a)$ and (8) are not applicable.

The curve for ice at $-20°$ c. in Fig. 1 when $x = 1$ cm. is intermediate, as would be expected, but it will be noted that, when x is varied, as in Fig. 3, the curve for $x = 1$ mm. is similar in character to that for $-50°$ c. and $x = 1$ cm., while the curve for $x = 1$ m. is similar in character to that at $20°$ c. for $x = 1$ cm. This is solely because of the influence of x on rates of diffusion, as given in eqn. $(3a)$. Rates of molecular distillation are independent of x, as shown by eqn. (8) and illustrated by the curves for $-20°$ c.

For ice at $-80°$ c. as in Fig. 2, with a vapour pressure of the order of 10^{-4} mm., the limiting eqn. $(3a)$ and (8) are clearly not of much use, and w remains nearly equal to w_0 up to values of P which are considerably greater than Π. It is not difficult to show that, when $\dfrac{k_1}{w_0 x} \gg 1$, as is the case here, P_i is always much less than P, whence

$$\frac{k_1}{x} \cdot \log \left(\frac{P}{P - P_i} \right) \simeq \frac{k}{x} \cdot \frac{P_i}{P}$$

and eqn. $(7a)$ then reduce to

$$\frac{w_0}{w} = 1 + \frac{w_0 x}{k} \cdot \frac{P}{\Pi}. \qquad . \qquad . \qquad . \qquad . \quad (9)$$

Influence of Free Mean Paths.

In the case of ice at $-80°$ c., the mean free path, λ, of the water vapour molecules in air becomes greater than x while P is still much greater than Π.   Thus, at $0°$ c. and 1 atm.

$$\lambda \simeq 1 \times 10^{-5} \text{ cm,}.$$

whence $\lambda \simeq 1 \times 10^{-5} \times \dfrac{T}{273} \times \dfrac{760}{P}$ (P in mm.)

and therefore, at $-80°$ c.,

$$\lambda \simeq \frac{5 \cdot 4 \times 10^{-3}}{P},$$

i.e. $\lambda = 1$ cm. when $P = 5 \cdot 4 \times 10^{-3}$ mm.   This introduces a fundamental point which has thus far been ignored, since, if x is of the same order as λ, evaporating vapour molecules can reach the condensing surface before colliding with an air molecule.   Under such conditions, the diffusion coefficient, D, used in calculating k_1 of eqn. $(7a)$ and k of eqn. (9), loses its meaning.   The form of the correction to be adopted would be difficult to obtain on purely theoretical grounds, but an approximate method has been suggested by Fuchs.[3]   A concentration gradient of vapour through the surrounding air or other permanent gas cannot be set up by the processes of diffusion until evaporating vapour molecules collide with air molecules.   One can therefore postulate that the average effect is the same as if P_i were constant over a finite thickness, Δ, which is equal to, or of similar magnitude to λ, and that a normal diffusion gradient is established beyond this point.   In brief, eqn. $(7a)$ and (9) can be corrected by replacing x with $(x - \Delta)$.   The effect of this correction, assuming $\Delta = \lambda$, is shown in Fig. 2 by a dotted curve, the main point being that $w/w_0 = 1$ when $\lambda = x$.

Evaporation of Droplets.—Some experimental data which afford at least a partial confirmation for Fuch's theory have been provided by Bradley, Evans and Whytelaw-Gray,[4] measuring rates of distillation of liquid droplets in an enclosure lined with adsorbent charcoal (i.e., $\Pi_c = 0$).   According to Langmuir,[5] if evaporation is governed by diffusion, the rate of evaporation from a droplet of mass m, and radius a, into an infinite enclosure is given by

$$-\frac{dm}{dt} = 4\pi a^2 w = 4\pi a \cdot \frac{MD\Pi}{RT}$$

i.e. $w = \dfrac{MD\Pi}{RTa} = \dfrac{k\Pi}{aP}.$

This assumes $P \gg \Pi$, as was always the case in Bradley's experiments and is analogous to eqn. (4).   Similarly, if w approaches w_0, Π must be replaced by P_i, and we derive an equation analogous to eqn. (9)

$$\frac{w_0}{w} = 1 + \frac{w_0 aP}{k\Pi}.$$

Suppose now that correction be made for the Fuchs layer, Δ.   Then diffusion takes place from a sphere of radius, $(a + \Delta)$, whence

$$-\frac{dm}{dt} = 4\pi a^2 w = 4\pi(a + \Delta) \cdot \frac{MDP_i}{RT}$$

i.e. $w = \dfrac{(a + \Delta)kP_i}{a^2 P}$

[3] Fuchs, *Physik. Z. Sowjet.*, 1934, **6,** 224.
[4] Bradley, Evans and Whytelaw-Gray, *Proc. Roy. Soc. A*, 1946, **186,** 368.
[5] Langmuir, *Physic. Rev.*, 1918, **12,** 368.

and
$$\frac{w_0}{w} = 1 + \frac{w_0 a^2 P}{(a + \Delta)k\,\Pi}.$$

Bradley has shown that an equation of this type accords with his results.

Influence of Correction.—The correction for λ cannot become appreciable till λ becomes comparable with x. Now, in general, even for larger molecules, λ at 760 mm. and the distillation temperature is of the order of 10^{-5} to 10^{-6} cm., while x is of the order of cm., whence λ cannot become comparable to x until P is less than 10^{-3} to 10^{-4} mm. On the whole, therefore, we can distinguish two cases.

(i) If Π is well above 10^{-4} mm., diffusion no longer controls when the correction becomes effective, so that corrections of x are immaterial. Eqn. (7a) can then be applied as they stand.

(ii) If Π is of the order of 10^{-4} mm. or less, $\lambda = x$ when $P < \Pi$, so that the correction must be applied. As eqn. (7a) reduce to eqn. (9) under these conditions, the equation to be applied is

$$\frac{w_0}{w} = 1 + \frac{w_0(x - \Delta)P}{k\,\Pi}. \qquad . \qquad . \qquad . \qquad (10)$$

Discussion.

In general, distillation or sublimation will be carried out at the highest practicable temperature, since the increase in vapour pressure favours rapid distillation; but temperatures are often limited in practice by danger of decomposition. The usual procedure for liquids has been, and will continue to be, to reduce pressure till boiling takes place at a safe temperature, since this only requires simple apparatus and gives high rates of distillation. Ebullition, however, possesses some distinct limitations. To avoid splashing, the condenser must be at some distance from the boiling liquid and, since vapour is transferred by flow instead of by diffusion, the condenser must be placed between boiler and vacuum pump. Now, at very low pressures, the volume of vapour produced is so great that (i) frothing and splashing tend to be excessive, (ii) the frictional losses between boiler and condenser are very appreciable, compared with the pressure maintained in the receiver by the vacuum pump. This is recognised in modern apparatus by use of wide passages for flow of vapour, but, even so, it is found that, no matter how small the pressure maintained by the vacuum pump, the pressure in the boiler might remain as high as 5 mm. Thus, if the liquid cannot safely be heated until its vapour pressure exceeds 5 mm., it cannot be boiled. In addition to this, nucleation and growth of vapour bubbles does not take place easily at very low pressures, and boiling may not occur at all, particularly in liquids with high viscosities.

It is in such cases that evaporative distillation is employed. The condensing surface is brought into the same space as the evaporating surface, and the whole space is evacuated to a uniform, small pressure, generally small enough to bring about the change from normal to molecular evaporative distillation. With this arrangement, boiling must clearly be avoided. Rates obtainable by this method may be compared with ebullition. A good overall heat-transfer coefficient to boiling water is 700 B.t.u./ft.^{2}/hr./$^\circ$F., which, even at a temperature difference of 100° F., corresponds only to a distillation rate of about 1×10^{-2} g./sec./cm.^{2} of heating surface, i.e. it is similar to w_0, per cm.^{2} of evaporating surface, for ice at -20° c.

It can be seen that the most important quantity in distillation at a given temperature, T, is the saturation vapour pressure, Π, and three cases will be considered, namely, (i) Π is of the order of 10^{-4} mm. or less, (ii) Π is of the order of 10^{-2} mm. or more, (iii) Π is greater than 1 mm.

(i) Molecular distillation first proved a useful technique for oily liquids of very low volatility, which could not be distilled by boiling. The considerations of the previous section show that a maximum rate of distillation is achieved by decreasing P until λ is of the same order as the distance between the evaporating and condensing surfaces, i.e. it is desirable to decrease pressures to 10^{-3} to 10^{-4} mm. If this is done, no matter how small the value of Π, distillation rates should not be very sensitive to variations in either P or x.

These factors are familiar in design of large-scale molecular distillation for non-volatile oils. It is necessary now to stress that quite other considerations apply for more volatile substances.

(ii) In the first place, when Π is greater than 10^{-2} mm., mean free paths can play no part in the character of the distillation or upon design. Again, if w is to approach w_0, P must be reduced well below Π, and, in fact, conditions must be reached where eqn. (8) can be used. Consideration of this equation shows that, if $w = 0.8\ w_0$ can be accepted as a reasonably high value for w, it is only necessary to decrease P to $0.2\,\Pi$, and that there is little point in proceeding to lower values, e.g. a decrease to $0.1\ \Pi$ would only increase w to $0.9w_0$. Further, when eqn. (8) is obeyed, distillation rates are quite unaffected by x.

(iii) When Π is greater than 1 mm., the same considerations apply as in (ii), but values of w_0 are so great that it is not necessary for w to approach equality with w_0. It would be desirable to utilise the rapid increase in w when $P = \Pi$, but there is little point in using much lower values of P. It is true that the actual values of w when $P = \Pi$ are sensitive to changes in x, as shown in Fig. 3, but the differences are greatly reduced if P is made a little less than Π.

In brief, molecular distillation is not necessarily limited to liquids of extremely low volatility. For substances with vapour pressures over 10^{-2} mm., it offers a possibility of very rapid distillation without use of very low pressures, and is more or less independent of the space between evaporating and condensing surfaces; though, of course, the design must ensure that evaporating molecules can be effectively removed by collision with the condensing surface. The main practical limitation is that P must be decreased somewhat below Π, and, in the case of most liquids, this would at once cause boiling to take place.

This limitation does not apply to sublimation of solids. In fact, the only limitations in this case seem to be the design problems involved in rapid transfer of heat into the solid being sublimed and in scraping the solid sublimate from the condenser surface. The outstanding application is " freeze-drying," as in sublimation of ice from penicillin preparations at $-20°$ c. to $-30°$ c. ; and here, as to be expected, the gap between evaporating and condensing surfaces does not appear to be critical, and it is not necessary to use particularly low pressures. From Fig. 3, it should not be necessary to go below 0.1 mm., and it would appear that the vacuum pump used is designed to give 0.01 mm. without load.[6]

[6] *Ind. Chem.*, 1945, 663.

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