

ON INDUCED EVAPORATION AT A MERCURY SURFACE

BY G. S. TRICK AND SIR ERIC RIDEAL

Chemistry Dept., King's College, Strand, London, W.C.2

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The rates of evaporation of benzophenone have been studied both *in vacuo* and in various pressures of nitrogen. From the data, the accommodation coefficient and its temperature dependence have been determined. Benzophenone spreads on mercury to form an expanded monolayer. Owing to evaporation from the monolayer, a bead of benzophenone in contact with a clean mercury surface evaporates more rapidly than when it is withdrawn from the surface. These specific rates of evaporation and the energies involved have been evaluated.

Substances which possess positive spreading coefficients will spread over a liquid surface until the crystal of solid or lens of liquid attains equilibrium with a monolayer exerting at any temperature a fixed spreading pressure. Such spreading coefficients have been measured at aqueous surfaces for a number of organic substances¹ and a few determinations have been made on mercury.² If the substance has an appreciable vapour pressure, the rate of loss of weight of the small crystal can be measured and, further, if the adhesion of the spread monolayer to the substrate is not too great, evaporation will take place also from the monolayer. For relatively low adhesive forces and rapid evaporation, we might imagine the case where the molecules leaving the crystal or lens and spreading over the liquid surface evaporate before they can reach the confines of the surface. Under these conditions no sensible spreading pressure can be built up and the apparent rate of evaporation of the crystal on the liquid surface should materially increase. The following experiments were made to see whether these conditions could be fulfilled.

For experiments on spreading on glass Volmer and Mahnert³ used benzophenone. Benzophenone is especially suitable for such an investigation since it has a vapour pressure of the right magnitude to enable its rate of evaporation to be measured.

EXPERIMENTAL

The essential parts of the apparatus are shown in fig. 1. The vacuum system consisted of a two-stage mercury diffusion pump backed by an Edwards 2S20 rotary oil pump. Pressures were measured on a McLeod gauge.

The process of purification of the mercury and production of a clean surface was identical with that employed by Kemball.⁴ The mercury was treated by aeration with sulphuric acid and ferrous sulphate, washing, drying, filtration and slow distillation before introduction to the mercury still M for distillation into the cup C. Benzophenone was purified by a double short-path sublimation to produce a product with a sharp melting point.

Losses in weight were recorded by means of a simple microbalance consisting of a fine uniform glass fibre B about 12 cm long. The displacement of the beam was directly proportional to the load and the sensitivity was 5.58×10^{-4} g/mm at 20° C. The deflection of the beam was measured with a travelling microscope, readings being reproducible to 0.02 mm. Hence, a change in weight of 1.12×10^{-5} g could be measured. Periodic checks were made on the sensitivity to ensure that the beam did not fatigue.

Attempts to prepare crystals of benzophenone of the proper size and strength were not successful. Hence, beads of benzophenone were prepared by first making a round ball on the end of a fine glass fibre. This ball was then repeatedly dipped into liquid benzophenone in contact with the solid phase. With practice and proper care it was

possible to prepare round beads with quite smooth surfaces when viewed under a low-power microscope. Any excess benzophenone adhering to the glass stem could be washed off. The size of the beads was measured with a travelling microscope and varied from 0.150 cm to 0.200 cm in diameter.

The experimental cell was enclosed in an air bath, the temperature being controlled to 0.1°C . To ensure that during an experiment the mercury was in thermal equilibrium with the air bath, a thermocouple well enabled the temperature of the mercury to be measured. The cold finger F could be introduced directly above the evaporating bead and the mercury seal S avoided the necessity for grease.

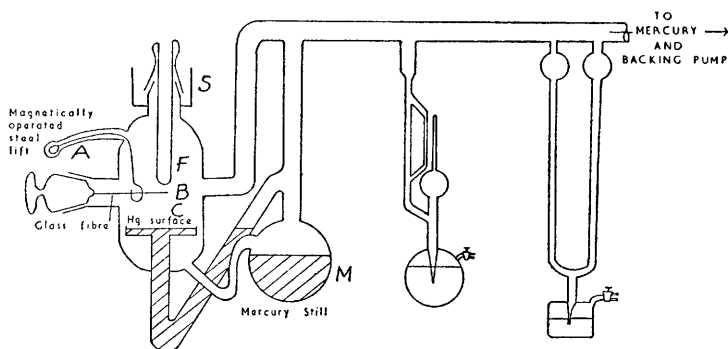


FIG. 1

Initially, mercury was distilled through the apparatus for several days to remove all volatile impurities. In a typical experiment the apparatus was evacuated to 10^{-4} to 10^{-5} mm Hg and mercury distilled over for 1 h. Dry air was admitted to the apparatus and the bead of benzophenone introduced by removing the cold finger and inserting the bead from above, hooking it over the end of the microbalance. This operation usually required about 1 min. The cold finger was replaced and the system again evacuated. When the pressure had again reached a low value, more mercury was distilled over and the liquid air was poured into the cold finger. In some cases a Dry Ice + acetone mixture was employed and found to give the same results. By means of the magnetically operated arrangement A consisting of a glass-enclosed iron core at one end of a silk thread and a loop of wire at the other end, which encircled the microbalance beam, it was possible to push the end of the microbalance down until the bead of benzophenone touched the mercury surface. Evaporation was allowed to proceed for a given time, usually 5 min, and then the bead was withdrawn, the microbalance allowed to hang free of the wire loop and the deflection measured. The measurement required 1 min and then the process was repeated.

We also required information on the rate of evaporation of a benzophenone bead *in vacuo*. Hence, a number of experiments were made with different size beads over a temperature range from 15°C to 25°C . In order to investigate the effect that any self-cooling of the bead could have on the experimental results, a number of measurements were made on the rate of evaporation in various pressures of nitrogen. In these experiments a cup of silica gel was employed in place of the cold finger and pressures measured on a mercury manometer and a McLeod gauge.

RESULTS

EVAPORATION OF BENZOPHENONE *in vacuo*

A typical experimental curve for the loss in weight of a bead of benzophenone evaporating in a vacuum is shown in fig. 2. It may be seen that the loss in weight is linear with time initially but that the rate shows tendencies to decrease. The theory of the factors affecting the rate of evaporation of a droplet and solid bead has been discussed by Langmuir,⁵ Fuchs,⁶ and Bradley *et al.*⁷ and the experimental results with benzophenone may be examined in this light.

From a consideration of Stephan's theory of diffusion, Langmuir concluded that when small spheres of liquid evaporate in air, they do so in such a manner that the rate

of change of surface with time is constant. The following equations represent his conclusions :

$$-dm/dt = 4\pi a Y C_0 m_2 / P, \quad (1)$$

$$-ds/dt = 8\pi Y C_0 m_2 / P \rho. \quad (2)$$

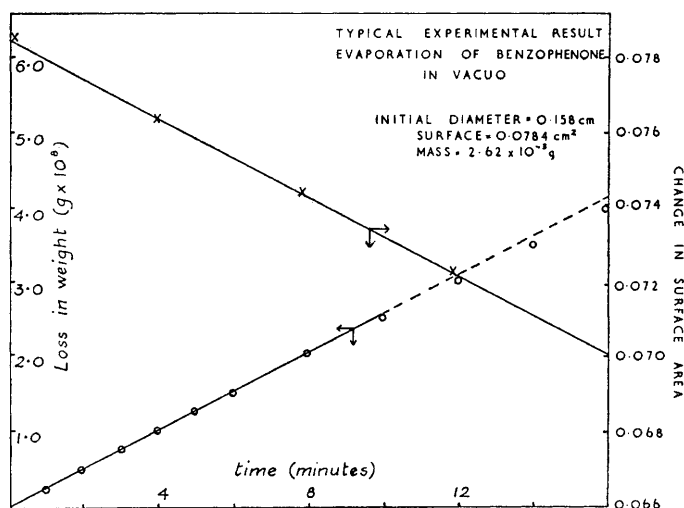


FIG. 2

It became evident, however, that at very low pressures these relations cannot be adequate, since the rate of evaporation would become greater than the vacuum rate. Bradley *et al.* have found that the following relations express the rate of evaporation of droplets of various liquids^{7, 8} and solid beads of sulphur.⁹

$$-\frac{dm}{dt} = \frac{4\pi a C_0 m_2}{\frac{1}{\alpha v \alpha} + \frac{P \alpha}{Y(a + \Delta)}} \rightarrow 4\pi a^2 v C_0 m_2, \text{ as } P \rightarrow 0, \quad (3)$$

$$-\frac{ds}{dt} = \frac{8\pi Y m_2 C_0}{P \rho} \left\{ \frac{1}{\frac{y}{P a v \alpha} + \frac{a}{a + \Delta}} \right\} \rightarrow \frac{8\pi a v \alpha C_0 m_2}{\rho}, \text{ as } P \rightarrow 0. \quad (4)$$

In the above relations,

- m = mass of sphere,
- a = radius of sphere,
- s = surface area of sphere,
- t = time,
- D = diffusion coefficient of evaporating molecules,
- m_2 = mass of evaporating molecule,
- C_0 = concentration of vapour at saturation,
- Δ = distance travelled by evaporating molecule before collision,
- $Y = PD$ by definition,
- ρ = density of sphere,
- $v = (kT/2\pi m_2)^{1/2}$,
- α = condensation coefficient.

In fig. 2 is also shown the rate of change of surface for the same bead. It will be noted that, while the rate of loss of mass shows a definite falling off with time, as expected from eqn. (3), the surface against time graph remains essentially linear since, from eqn. (4), ds/dt is less sensitive to the decrease in the radius of the bead as evaporation proceeds. For convenience, all rates of evaporation were calculated from a mass against time relationship, taking the slope of the initial portion of the curve where the radius is essentially constant.

TABLE 1.—EVAPORATION OF BENZOPHENONE

temp. °C	diameter of bead cm	dm/dt g/sec $\times 10^7$	dm/dt g/cm ² sec $\times 10^6$	dm/dt eqn. (3) g/cm ² sec $\times 10^6$	condensation coefficient α
25	0.171	8.82	9.64	30.1	0.321
25	0.199	11.8	9.51	30.1	0.317
22.5	0.156	5.21	6.78	20.5	0.331
20	0.158	4.31	5.48	15.1	0.363
18	0.176	3.99	4.09	11.7	0.349
18	0.184	4.37	4.12	11.7	0.352
15	0.173	2.97	3.15	7.87	0.402

TABLE 2.—EVAPORATION OF BENZOPHENONE IN NITROGEN
Temp. 25° C

diameter of bead cm	$-dm/dt$ g/sec $\times 10^7$	P cm	$1/P$ cm ⁻¹	q_0 g/sec $\times 10^7$	$\frac{q_0}{q}$	$\frac{q_0}{q} - \frac{a}{a + \Delta}$
0.199	2.01	1.88	0.532	1.97	0.98	(- 0.015)
0.196	4.00	0.92	1.09	3.94	0.98	(- 0.01)
0.198	4.60	0.80	1.25	4.62	1.00	(0.01)
0.194	5.47	0.64	1.56	5.64	1.03	(0.04)
0.173	5.77	0.02	50	15.80	2.74	1.90
0.172	8.33	0.0078	128	40.4	4.86	4.20
0.171	8.80	0.0020	500	158.5	18.0	17.67

In table 1 are summarized the results of a number of experiments at different temperatures. In column 5 are shown the theoretical rates of evaporation calculated from eqn. (3) assuming a condensation coefficient of unity. The ratio of the experimental rate to this value yields the condensation coefficients in the last column.

In fig. 3 are reproduced the results of Volmer and Kirchoff¹⁰ on the vapour pressure of benzophenone in the temperature range 15–25° C. On the same graph is plotted the apparent evaporation pressure p_e , where $p_e = \alpha p$, p being the equilibrium vapour pressure. The data of Volmer and Kirchoff give a heat of sublimation of 22,500 cal/mole, whereas the activation energy for evaporation is 20,500 cal/mole. Hence, it would appear that if the bead consists of rhombic benzophenone, the condensation coefficient has a negative activation energy of 2000 cal and would only become unity at – 50° C.

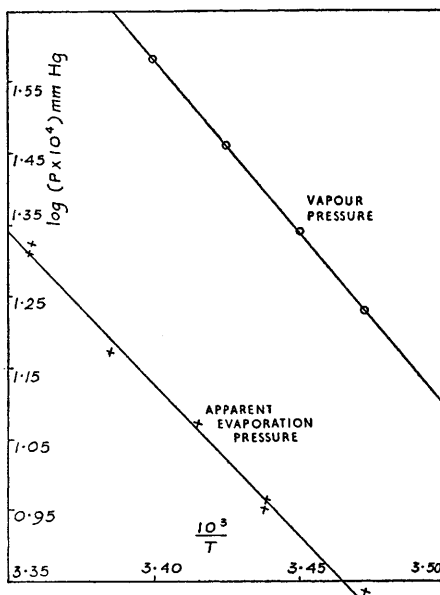


FIG. 3

EVAPORATION OF BENZOPHENONE IN NITROGEN

The experimental results for a number of different beads in various pressures of nitrogen are shown in table 2. From these results it is possible to calculate the condensation coefficient and have an independent check on the value obtained from the rate of evaporation *in vacuo*.

At relatively high pressures of nitrogen, i.e. in the Langmuir region, both Δ and D are small and eqn. (3) becomes identical with eqn. (1). Hence, by plotting $-dm/\alpha dt$ against $1/P$ a straight line should result, enabling D to be

determined. The data from the first four experiments in table 2 are plotted in fig. 4, and it is found that $D = 0.0602 \text{ cm}^2 \text{ sec}^{-1}$ at 76 cm of mercury.

At lower pressures where Langmuir's relation is not adequate we may define a quantity $q_0 = dm/dt = 4\pi aDC_0m_2$, i.e. q_0 represents the value of $-dm/dt$ at any particular pressure supposing that the rate did obey eqn. (1). If q is the actual rate of evaporation at the same pressure, then from eqn. (3),

$$\frac{q_0}{q} - \frac{a}{a + \Delta} = \frac{D}{av\alpha} = \frac{Y}{Pav\alpha}. \quad (5)$$

Hence, a plot of the left-hand side of eqn. (5) against $1/P$ should be a straight line, from the slope of which α may be calculated. The required quantities are shown in table 2. The value of Δ was calculated from the relation

$$\Delta = kT/\pi S_{12}^2 P,$$

where S_{12} , the collision radius for benzophenone molecules and nitrogen, is calculated from the equation

$$D = \frac{2}{3} \frac{1}{(1 + \alpha_{21})} \frac{1}{\pi n S_{12}^2} \left[\frac{2kT(m_1 + m_2)}{\pi m_1 m_2} \right]^{\frac{1}{2}},$$

where n is number of molecules per unit volume, m_1 and m_2 the masses of nitrogen molecules and benzophenone molecules and $\alpha_{21} = 0.33$. It is found that $S_{12} = 5.32 \times 10^{-8}$ cm at 25° C.

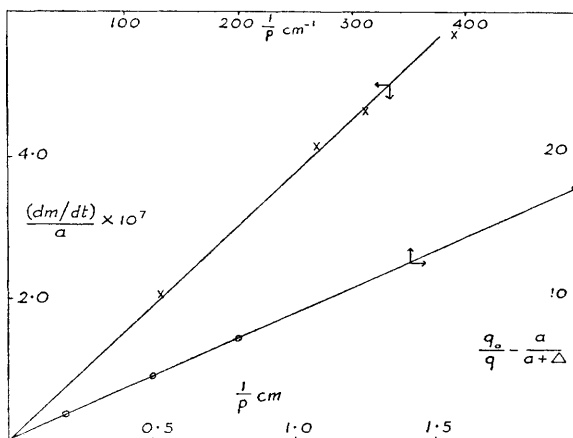


FIG. 4

In fig. 4 are plotted the values from table 2 in the form of eqn. (5) and from the slope it is found that $\alpha = 0.324$, in good agreement with the value shown in table 1, obtained from the rate of evaporation *in vacuo*. Hence, it may be concluded that any self-cooling which is occurring does not appreciably affect the experimental results.

EVAPORATION OF BENZOQUINONE IN CONTACT WITH MERCURY

When the benzoquinone bead was allowed to evaporate while touching the centre of a mercury surface 2.2 cm in diameter, the overall rate of loss in weight was increased. The problem arose as to the manner of calculating the amount of evaporation which could be attributed to the presence of the mercury surface. The chief difficulty was that the mercury, in contact with the bead of benzoquinone or in close proximity with it, would effectively decrease the surface area of the bead from which free evaporation into the vacuum could take place. It was found that when a bead of lauric acid was employed in place of benzophenone the presence of the mercury surface caused a decrease in the overall rate of evaporation. This would appear to be due to the "shielding" effect of the mercury surface, and if it is assumed that lauric acid does not spread on a mercury surface, or, as will be indicated later, that spreading does occur but that the mercury + lauric acid adhesion energy is sufficient to prevent any appreciable evaporation of the film, then the mercury surface decreased the surface area of the bead by $27 \pm 2\%$. This quantity was independent of the size of the bead and of the temperature, the latter fact

being good proof that if any evaporation of the lauric acid films was taking place, the quantity involved was not sufficient to be detected by the experimental arrangement, and hence will not affect the results. It thus seems reasonable to assume that with benzophenone also, the mercury effectively covers 27 % of the surface area of the bead.

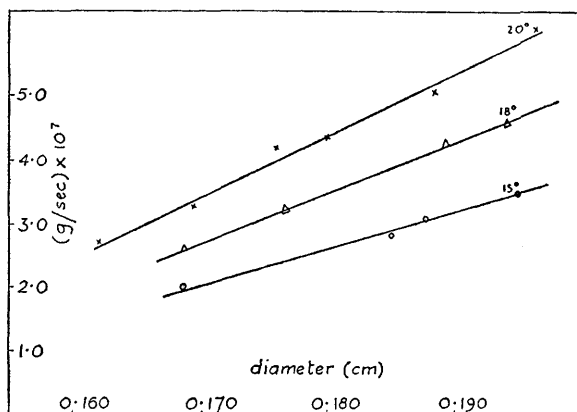


FIG. 5.

The amount of evaporation caused by the presence of the mercury surface was thus calculated by measuring the overall rate of evaporation and subtracting a quantity equal to 73 % of the rate of evaporation which would be expected from a bead of the same size evaporating in a vacuum, using smoother values of the apparent evaporation pressure taken from fig. 3.

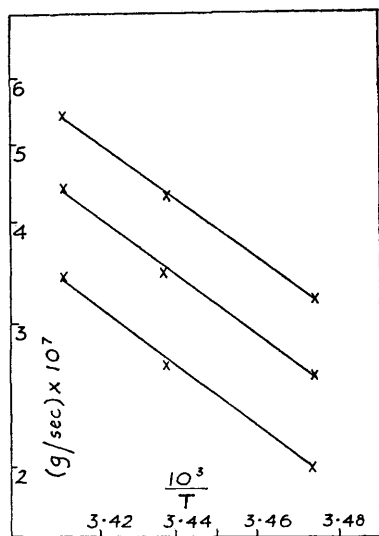


FIG. 6

It was found that the rate of evaporation due to the mercury depended upon the size of the bead of benzophenone. In fig. 5 are shown the experimental results over the temperature range 15° to 20° C. Experiments were not made at higher temperatures since the rapid decrease in the size of the bead would introduce considerable errors. In fig. 6 are shown the activation energies for the points from the best lines drawn in fig. 4, taken at three different diameters 0.190 cm, 0.180 cm and 0.170 cm. The values for the activation energies are 16,700 cal/mole, 17,350 cal/mole, and 17,600 cal/mole respectively.

A number of experiments were made in an attempt to determine the extent to which the film spread over the mercury surface before evaporating. The results were erratic, however, mainly due to the difficulty in maintaining the point of contact of the bead near the centre of the mercury surface. However, it was established that when the surface

was decreased from 2.2 cm to 1.0 cm in diameter and the bead kept near the centre of the surface, no change in the amount of evaporation from the mercury surface could be noted. All evidence pointed to a rapid evaporation of the benzophenone film from the mercury and the results shown in fig. 5 actually include a correction factor to allow for the 1 min in every 6 in which the benzophenone bead was removed from contact with the mercury so that its mass could be measured.

In two experiments a bead of lauric acid was placed in contact with the mercury surface and then experiments made with benzophenone in the usual manner. In such cases the amount of evaporation from the mercury was approximately 40 % of the normal value.

DISCUSSION

EVAPORATION OF BENZOPHENONE *in vacuo* AND IN NITROGEN

In the interpretation of the experimental results on the rate of evaporation of benzophenone *in vacuo* something must be said on the possibility of self-cooling appreciably affecting the data. However, the good agreement obtained between the condensation coefficient obtained from the rate of evaporation *in vacuo* and that obtained from evaporation in nitrogen is good proof that self-cooling is not serious since considerable temperature equilibration should occur between the bead and the walls of the experimental vessel, even at pressures of 0.002 cm Hg. Experiments with nitrogen were only made at the highest temperature (25° C) but at this temperature any self-cooling would be more serious than at lower temperatures.

Another possible source of error which must be considered is the effect that the relatively large quantities of mercury vapour present can have upon the velocity of evaporation of the benzophenone. It might be expected that the mercury atmosphere would tend to decrease the rate of diffusion of the evaporating molecules away from the bead and hence decrease the rate of evaporation. However, the magnetic arrangement A enabled the rate of evaporation to be measured with the bead at different distances intermediate between the cold surface and the mercury surface and no variation in rate was observed. Since a considerable concentration gradient should exist between the two surfaces, the mercury does not appear to cause any serious errors.

There was no indication that the solid bead contained any form of benzophenone other than the rhombic form, and hence vapour pressure data for this form have been used. Although in most cases the bead was used about 1 h after preparation, beads kept for several hours or days gave identical rates of evaporation. Hence, the method of preparing the bead does not appear to produce any metastable form of benzophenone.

The values of the condensation coefficients are all considerably less than unity and imply some impedance to the condensation of vapours on striking the surface of the bead. Low values of α are usually associated with an orientation factor θ and an energy barrier to condensation E so that $\alpha = \theta \exp(-E/RT)$. However, with benzophenone we note that α has a negative temperature coefficient. It would appear likely that the surface of benzophenone is covered by a mobile layer of molecules of random orientation which effectively decrease the number of crystalline sites or surface lattice kinks available for condensation. As the temperature is decreased the surface layer becomes more rigid and the condensation coefficient increases. The retarding effect of the mobile layer to condensation would appear to be associated with the polar property of the benzophenone molecule since Bradley and Shellard have observed condensation coefficients near unity for both solid and liquid hydrocarbons. In any case, the condensation coefficient may be expressed by the relationship

$$\alpha = 0.011 \exp(2000/RT)$$

although the significance of the constants involved cannot be stated with any exactness.

EVAPORATION OF BENZOPHENONE IN CONTACT WITH MERCURY

There seems no question but that the increased rate of loss of weight of a benzophenone bead when in contact with mercury is due to a surface effect followed by evaporation. The results could be explained by dissolution of benzophenone in mercury but Volmer and Mahnert³ were not able to detect any evidence for solution. The experimental results were in no way dependent on the amount of freshly distilled mercury present in the cup; some effect would be expected if any question of solution arose. In addition, the action of lauric acid in retarding the phenomena observed shows that we are definitely dealing with a surface

effect. We thus have a picture of the mercury behaving as a surface over which the benzophenone will spread. The film formed will then evaporate and be replenished by further spreading from the solid.

The influence of the size of the bead on the amount of evaporation, as shown in fig. 5, may be attributed to an increase in the length of the mercury + benzophenone + air interface as the bead increases in size. The experimental arrangement was such that the benzophenone bead floated freely on the mercury surface and hence the depth of penetration depended on the mass of the bead. The accuracy of the results and the small range of diameters investigated did not justify a check to be made on the relation between the rate of removal of benzophenone molecules from the bead and the length of the triple interface.

Since the rate of evaporation was not influenced by decreasing the diameter of the mercury surface from 2.2 cm to 1.0 cm it would appear that the benzophenone film does not spread to an area greater than this diameter before evaporation occurs. This fact indicates that the slow step in the overall process is the removal of the benzophenone molecules from the bead rather than the removal of the film from the surface. Thus, the activation energies obtained from fig. 6 will be associated with this slow step. The small change in activation energy with bead size is within the experimental error and the average value is 17,200 cal. Since the activation energy for evaporation in a vacuum is 20,500 cal, the effect of the mercury surface is to decrease by 3300 cal the energy required for removal of 1 mole of benzophenone from the bead. Energy will, of course, be required in the evaporation of the benzophenone from the mercury surface. This must be smaller than 17,500 cal.

Because of the experimental arrangement used, the benzophenone film formed is undoubtedly a gaseous type with practically no cohesion between the various benzophenone molecules of the film. The spreading of the film away from the bead is not opposed to any extent by the presence of other benzophenone molecules and since the film never completely covers the mercury surface no appreciable surface pressure will be built up to cause closer packing of the film.

The nature of the film of benzophenone formed is undoubtedly affected to some extent by the evaporation of mercury from the mercury surface while an experiment is in progress. Because of this evaporation, the benzophenone actually spreads over a turbulent surface which is being continually renewed by evaporation of mercury. This evaporation possibly increases to some extent the rate at which benzophenone molecules are removed from the immediate vicinity of the solid bead but it will not affect the overall energetics of the process. In order to investigate a stable film which spreads to a measurable area over the mercury, it would be necessary to employ a solid of higher vapour pressure and study the evaporation in an inert atmosphere in the Langmuir region.

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