varying density range. In subsequent publications, the dielectric constants of the other well-known mixtures such as aliphatic alcohols with water, alcohols with dioxane, and alcohol–alcohol systems will be investigated using our extended model for mixtures.

Rupture of Thin Liquid Films Due to Spontaneous Fluctuations in Thickness

A. Vrij and J. Th. G. Overbeek

Contribution from the van't Hoff Laboratory, University of Utrecht, Utrecht, Netherlands. Received November 27, 1967

Abstract: The surfaces of thin liquid films are slightly corrugated because of thermal fluctuations. These corrugations show up in the light scattered by these films. It can be shown that corrugations having wavelengths larger than a critical wavelength will grow spontaneously, because of the action of van der Waals forces, and will cause the film to become rapidly thinner and break (or be stabilized as a black film, if sufficiently strong repulsive forces keep the two faces of the film separated). The critical wavelength $\Lambda_{crit} = [-2\pi^2\gamma/(d^2G/dh^2)]^{1/2}$, in which γ is the surface tension, G the Gibbs energy of interaction among the molecules per unit area of the film, and h the thickness of the film. The rate at which fluctuations above the critical wavelength grow depends on the viscosity of the liquid, and it can be shown that the combination of regular drainage and spontaneous growth of fluctuations leads to a critical thickness and a lifetime for the film of the same order as those found in experiments.

It is well known that Professor Debye had a vivid interest in fluctuation phenomena as manifested, *e.g.*, in light scattering. He also was interested and fascinated by the measurements of van der Waals forces between macroscopic bodies. It is therefore fitting that in this volume a paper is dedicated to his memory, which deals with a case where the combination of a fluctuation phenomenon and van der Waals forces leads to an explanation of the kinetics of breaking of thin films.

The ultimate lack of stability of foams and emulsions is not difficult to understand. These structures have a very large interfacial area, and decrease of this area is accompanied by a decrease in free energy. The mechanisms, however, by which this decrease in interfacial area is obtained, are less well understood. This is particularly true of the most efficient mechanism for coarsening foams and emulsions, *in casu*, the breaking of thin liquid lamellae between two foam bubbles or emulsion droplets. It appears as if at a "critical thickness" of the order of 0.1 μm these lamellae may become unstable and break suddenly. On the other hand, about 10 years ago de Vries[1] calculated that the energy of activation required to form a hole in a thin film is on the order of γh^2, where γ is the interfacial tension and h the thickness of the film. The film is not expected to burst until its thickness is down to a value for which the energy of activation for hole formation is a small multiple of the equipartition energy, kT, that is, for an interfacial tension of about 10 dynes/cm, down to about 20 Å.

A solution of this apparent paradox can be based upon the natural roughness of all interfaces. Although the existence of a surface tension tends to make the surface as flat as possible, thermal motions will cause a certain roughness. This roughness can be observed experimentally, because a surface that is not completely flat not only reflects but also scatters some of the light falling on it (see Figure 1).

The profile of the surface can always be represented as a sum of Fourier waves. Since each of these Fourier terms can be considered as an independent degree of freedom of the system, the average amplitude of each wave is fixed by the condition that the increase in surface Gibbs energy (surface tension multiplied by the increase in area) caused by this wave is just equal to the equipartition energy, $^1/_2kT$. The theory of surface light scattering has been given by Mandelstam[2] in 1913 and was further developed by Gans[3] (1924) and Andronow and Leontowicz[4] (1926). Experiments by Raman and Ramdas[5] (1925) and by a few others confirmed the theory, but the phenomenon was more or less forgotten, presumably as a consequence of the experimental difficulty caused by the simultaneous occurrence of bulk light scattering which is usually stronger than the scattering by the surface.

A few years ago, one of us[6] considered the possibility of calculating and measuring surface light scattering by thin liquid films. Here the bulk scattering is negligible, making experimentation easier. The theory is more complicated because of the optical interference of light scattered by the two surfaces of the thin films. But there is a third aspect which makes the investigation of

(1) A. J. de Vries, *Rec. Trav. Chim.*, 77, 383, 441 (1958).

(2) L. Mandelstam, *Ann. Physik.*, 41, 609 (1913).
(3) R. Gans, *ibid.*, 74, 231 (1924); 79, 204 (1926).
(4) A. Andronow and M. Leontowicz, *Z. Physik*, 38, 485 (1926).
(5) (a) C. V. Raman, *Nature*, 112, 281 (1923); (b) C. V. Raman and L. A. Ramdas, *Proc. Roy. Soc.* (London), A108, 561 (1925); A109, 150, 272 (1925); (c) L. A. Ramdas, *Indian J. Phys.*, 1, 29, 199 (1927); (d) C. V. Raman, *ibid.*, 1, 97 (1927).
(6) A. Vrij, *J. Colloid. Sci.*, 19, 1 (1964).
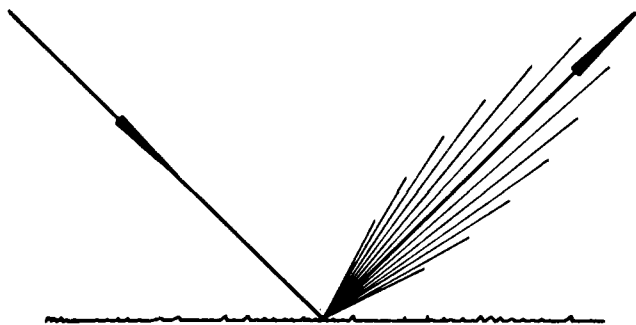
Figure 1. Reflection of light from a rough surface, accompanied by scattering.

Figure 2. Diagram showing why a molecule in a thin film is always attracted toward the thicker parts of the film. Molecule M experiences an uncompensated attraction to the right due to molecules in shaded area of figure.

scattering particularly attractive. When the film is very thin (less than 1000 Å), the shapes of the fluctuations in the two surfaces become correlated because of the molecular interactions in the film. This influences the light scattering, and, inversely, light scattering by thin films becomes a new and powerful tool for investigating these forces. Forces in thin films may be of several kinds. van der Waals (dispersion) forces are always present and will always tend to drive the molecules from thinner to thicker parts of the film, as is shown in Figure 2. If we consider a molecule, M, in a film, in which the thickness increases from left to right, we can easily see that the attraction by all molecules left from M is compensated exactly by the mirror image of that part of the film, leaving parts of the thicker film (cross-hatched in Figure 2) to attract M to the right. It is obvious that this effect is only important if the range of the attractive forces is larger than half the thickness of the film.

Other forces that often play a role in thin films are connected with the presence of soaps or other foam stabilizing substances. Their molecules are adsorbed at the interfaces liquid–gas, and, if they are dissociated into ions they create a surface charge. The surface charges on both sides of the film repel one another and thus favor thicker films, or, if the adsorbed molecules are nonionic, but contain a fairly bulky hydrophilic group, such as a polyethylene oxide chain, they prevent the aqueous core of the film from becoming thinner than twice the diameter of this bulky group and so lead to a steep rather short-range repulsion. The so-called black soap films—black, because interference between light reflected from the front side and that reflected from the back side leads to nearly complete extinction of the reflected light—are structures in which the different forces have come to an equilibrium. Since black films form spontaneously from the thicker, colored ones, the Gibbs energy connected with its surfaces is smaller than twice the normal surface Gibbs energy (surface tension). This causes the black film to be attached to the bulk of the liquid with a finite contact angle as predicted by Princen and Mason,[7] by Deryagin, Martynov, and Gutop,[8] by Vreeman,[9] and as confirmed recently in experiments by Mysels, Huisman, and Razouk.[10]

(7) H. M. Princen and S. G. Mason, J. Colloid Sci., 20, 156 (1965).
(8) B. V. Deryagin, G. A. Martynov, and Yu. V. Gutop, "Research in Surface Forces," Vol. 2, B. V. Deryagin, Ed., Consultants Bureau, New York, N. Y., 1966, pp 9–16.
(9) H. Vreeman, private communication.
(10) K. J. Mysels, H. F. Huisman, and R. I. Razouk, J. Phys. Chem., 70, 1339 (1966).
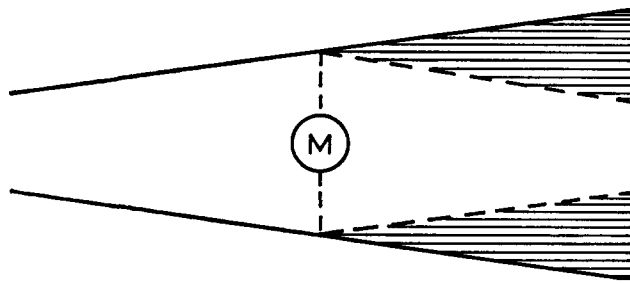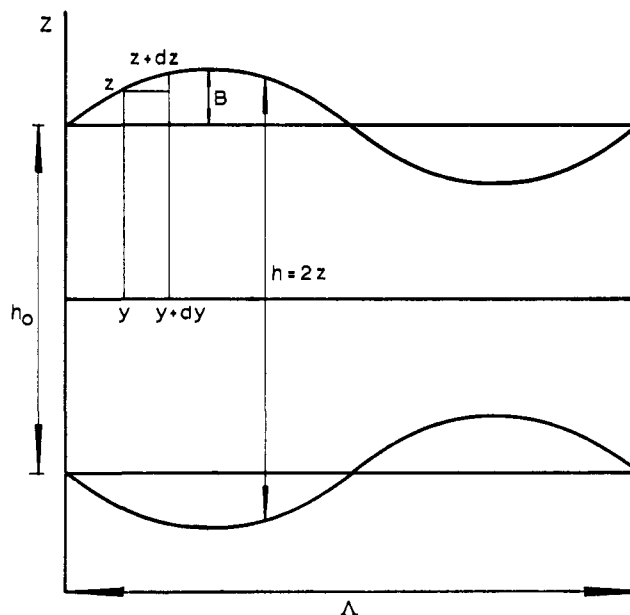
Figure 3. One of the Fourier components of the corrugations of a thin film of average thickness, h_0. Wavelength = Λ. Amplitude of the wave on each surface = $B \sin (2\pi y/\Lambda)$.

Critical Wavelength for Fluctuations Leading to Spontaneous Growth

We now return to the surface corrugations but take the interaction forces into account. As mentioned above, the surface tension will act against the corrugations, but the van der Waals forces will favor disproportionation of a film into thin and thick parts, and it is conceivable that for certain types of deformations the increase in surface Gibbs energy will be more than compensated by the total decrease in van der Waals energy. Such deformations would grow spontaneously in amplitude and lead to rupture of the films or to its stabilization as a black film, if the repulsive forces are strong enough. This theory for film rupture has first been proposed by Scheludko[11] and has been further developed and connected with surface light scattering by one of us.[12]

We consider an area of the film of 1 cm long and Λ cm wide with a deformation as drawn in Figure 3, which is one of the many Fourier components into which the total corrugation of the film can be split up. The Gibbs energy, ΔG, contained in this particular wave,

(11) A. Scheludko, Proc. Koninkl. Ned. Akad. Wetenschap., B65, 87 (1962).
(12) A. Vrij, Discussions Faraday Soc., 42, 23 (1966).

compared to a completely flat film of thickness, h_0, is

$$\Delta G = \text{extra area} \times \gamma + \text{extra interaction energy} \quad (1)$$

where γ is the surface tension.

The extra area on the two sides of the film is given by

$$2 \int_{y=0}^{y=\Lambda} \{[(dz)^2 + (dy)^2]^{1/2} - dy\} =$$

$$2 \int_0^\Lambda \left[\sqrt{1 + \left(\frac{dz}{dy}\right)^2} - 1\right] dy = \int_0^\Lambda \left(\frac{dz}{dy}\right)^2 dy \quad (2)$$

If $G(h)$ is the Gibbs energy of interaction per unit area among all the molecules in the film, the extra interaction energy in the wave form of Figure 3 is given by

$$\int_0^\Lambda \left[\frac{dG(h)}{dh}\Delta h + \frac{1}{2}\frac{d^2G(h)}{dh^2}(\Delta h)^2 \ldots\right] dy$$

in which $\Delta h = h - h_0$.

Since $z = z_0 + B \sin (2\pi y/\Lambda)$ and $h = h_0 + 2B \sin (2\pi y/\Lambda)$, the total extra Gibbs energy becomes

$$\Delta G = \gamma \int_0^\Lambda \left(\frac{dz}{dy}\right)^2 dy + \int_0^\Lambda \frac{dG}{dh} 2B \times$$

$$\sin\left(\frac{2\pi y}{\Lambda}\right) dy + \frac{1}{2} \int_0^\Lambda \frac{d^2G}{dh^2} 4B^2 \sin^2\left(\frac{2\pi y}{\Lambda}\right) dy =$$

$$\gamma B^2 \frac{4\pi^2}{\Lambda^2} \int_0^\Lambda \cos^2\left(\frac{2\pi y}{\Lambda}\right) dy + 0 +$$

$$2B^2 \frac{d^2G}{dh^2} \int_0^\Lambda \sin^2\left(\frac{2\pi y}{\Lambda}\right) dy \quad (3)$$

Consequently the total Gibbs energy is negative, and this particular fluctuation will tend to grow if

$$\gamma B^2 \frac{4\pi^2}{\Lambda^2} + 2B^2 \frac{d^2G}{dh^2} < 0 \quad (4)$$

or if

$$\Lambda > \Lambda_{\text{crit}} = [-2\pi^2\gamma/(d^2G/dh^2)]^{1/2} \quad (5)$$

In the particular case that $G(h)$ is essentially determined by van der Waals forces

$$G = -\frac{A}{12\pi h^2} \quad (6)$$

where A is the Hamaker–van der Waals constant (the relativistic retardation of the van der Waals forces being neglected here). In that case the critical wavelength becomes

$$\Lambda_{\text{crit}} = 2\pi\sqrt{\frac{\pi\gamma h^4}{A}} \quad (7)$$

and with $A = 10^{-12}$ erg and $\gamma = 10$ dyne/cm, this leads to

$$\Lambda_{\text{crit}} = 2\pi h^2 \sqrt{\frac{\pi \times 10^{13}}{\text{cm}^2}} = 0.35 \times 10^8 h^2 \text{ cm}^{-1} \quad (8)$$

or

$$\Lambda_{\text{crit}} = 0.35\left(\frac{h}{\mu\text{m}}\right)^2 \text{ cm} \quad (9)$$

Consequently, if h is 1 μm, Λ_{crit} is 0.35 cm.

On a macroscopic thin film with a linear dimension on the order of 1 mm or 1 cm, the critical wavelength

can be formed when the thickness has decreased below about 1 μm. For the thin lamella remaining between two oil drops in a creamed oil in water emulsion, however, where the droplet size itself may be only 1 μm or a few micrometers, the thickness has to decrease below 200 Å before fluctuations can make it unstable.

Rate of Growth of Fluctuations

Even if a combination of area and thickness is reached, where spontaneously growing fluctuations may form, the growing of such a fluctuation requires time on account of the viscous resistance against flow. The lifetime of a fluctuation will be long when its wavelength is only slightly larger than Λ_{crit} because in that case the driving force for growth is small. On the other hand, when the wavelength of the fluctuation is very large, it will grow slowly because the liquid has to be transported over large distances.

The rate of growth of fluctuations can be estimated quantitatively by considering displacement of liquid as viscous flow caused by the pressure gradients in the film. These pressure gradients are due to the curvature of the surfaces (capillary pressure) and to the thickness variations of the film (effect of interaction forces).

For small disturbances the excess pressure as compared with the pressure in a flat film is given by

$$\Delta P = \Delta P_{\text{cap}} + \Delta P_{\text{forces}} = -\gamma\frac{d^2z}{dy^2} + \frac{d^2G}{dh^2}\Delta h \quad (10)$$

For a film stabilized by even a small amount of surfactant adsorbed at the surfaces, the surface will be as good as stationary and the flow of liquid can be described as laminar flow between two fixed walls under the influence of the pressure gradient, or in equation form

$$\text{flow rate (volume/time)} = Q = -\frac{h_0^3}{12\eta}\frac{d(\Delta P)}{dy} \quad (11)$$

The conservation of volume requires that the change in thickness of the film with time is given by

$$\frac{\partial h}{\partial t} = -\text{div } Q = -\frac{dQ}{dy} = \frac{h_0^3}{12\eta}\frac{d^2(\Delta P)}{dy^2} \quad (12)$$

where η is the viscosity of the flowing liquid. Substituting ΔP from eq 10, using the relation between y, z, and h as given in Figure 3, and solving the differential equation thus obtained, we find

$$(h - h_0) = (h - h_0)_{t=0} \exp\left(\frac{t}{\tau}\right) \quad (13)$$

in which the characteristic time τ is given by

$$\tau = -\frac{3\eta\Lambda^2}{\pi^2 h_0^3}\left(\frac{2\pi^2\gamma}{\Lambda^2} + \left(\frac{d^2G}{dh^2}\right)_{h=h_0}\right)^{-1} \quad (14)$$

For $\Lambda < \Lambda_{\text{crit}}$, τ is negative, and the wave will be damped, but, if $\Lambda > \Lambda_{\text{crit}}$, τ is positive and the amplitude of the wave will grow. The wave growing most rapidly ($\tau = \tau_{\text{min}}$) has a wavelength

$$\Lambda(\text{most rapid growth}) = \Lambda_{\text{crit}}\sqrt{2} \quad (15)$$

Taking again only van der Waals forces (eq 6) into account, the characteristic time for most rapid growth is found to be

$$\tau_{\text{min}} = 96\pi^2\eta\gamma A^{-2}h_0^5 \quad (16)$$

Inserting the reasonable values $\eta = 0.01$ poise, $\gamma = 20$ dynes cm^{-1}, and $A = 10^{-12}$ erg into eq 16, the characteristic time, $\tau_{\min}$, is found to be about 1 week for $h = 1$ μm, about 1 sec for $h = 700$ Å, and 1 msec for $h = 175$ Å. Equation 16 with its dramatic dependence of $\tau_{\min}$ from h not only suggests the existence of a critical thickness at which a film starts to thin very rapidly, but also explains that this rapid thinning or breaking will be observed at a thickness of a few hundred angstroms.

Comparison with Experiments

A critical thickness for breaking of the film will be reached when the film is so thin that the rate of growth of fluctuations is faster than the thinning by other drainage processes. For large films, the drainage processes may be rather complicated, but small circular films (radius a few tenths of a mm) drain quite regularly, as shown by Scheludko, Exerowa, and Kolarov.[13] The drainage is a viscous flow of the liquid, with the surface layers stagnant, driven by the pressure difference, P, between the film and the border to which it is attached. Reynolds[14] has given an equation for the rate of this process for a film of radius r.

$$\frac{d(h_0^{-2})}{dt} = \frac{4}{3\eta r^2} P \qquad (17)$$

Scheludko,[15] Frankel and Mysels,[16] and Platikanov[17] have given further discussions of this type of drainage. The critical thickness can now be found from the requirement that the total time of thinning of the film (approximately the sum of the time of drainage to a thickness, h_0, and the time in which the most rapidly growing fluctuation just reaches an amplitude h_0, so that the film just bursts) is a minimum. This requires finding the value of h_0, which we call h_m, for which

$$\frac{d}{dh_0}(t_{\text{drain}} + t_{\text{fluct}}) = 0 \qquad (18)$$

It can be shown[12] that the development of a fluctuation from its statistical average ($h - h_0 \simeq 1$ Å, neglecting for a moment the interaction forces) to the point of bursting ($h - h_0 \sim$ a few times 100 Å) requires only 5–7 times $\tau_{\min}$. Therefore we put

$$t_{\text{fluct}} = f\tau_{\min} \qquad (19)$$

with $f \sim 6$. As h_0 becomes smaller and smaller, the drainage time t_{drain} becomes longer, and the fluctuation time t_{fluct} becomes shorter. Figure 4, drawn for a drainage following eq 17 (with P and r constant) and a fluctuation growth according to eq 13 with $\tau = \tau_{\min}$ as given in eq 16, shows that for drainage times 3, 5, and 7.2 values of h_0 are reached equal to 0.5, 0.41, and 0.35, respectively, of the thickness at $t = 0$, and it shows clearly that the bursting time is shorter for drainage to $h_0 = 0.41$ than for drainage to either a larger or a smaller thickness. Figure 4 also shows that the average thickness of the film at the moment of bursting is somewhat smaller than h_m, since the film has continued

(13) (a) A. Scheludko, Proc. Koninkl. Ned. Akad. Wetenschap., B65, 76, 87 (1962); (b) A. Scheludko, Kolloid-Z., 155, 39 (1957); (c) A. Scheludko and D. Exerowa, ibid., 168, 24 (1960); (d) D. Exerowa and T. Kolarov, Ann. Univ. Sofia, Fac. Chim., 59, 207 (1964/65).
(14) O. Reynolds, Phil. Trans. Roy. Soc. (London), 177, 157 (1886).
(15) A. Scheludko, Kolloid-Z., 191, 52 (1963).
(16) S. Frankel and K. J. Mysels, J. Phys. Chem., 66, 190 (1962).
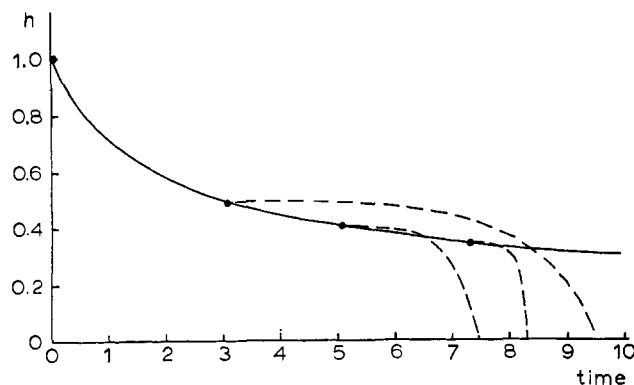(17) D. Platikanov, ibid., 60, 3619 (1964).

Figure 4. Combination of drainage (drawn line) following $d(h_{\text{init}}/h_0)^2/dt = 1$ with fluctuations (dotted lines) growing exponentially (eq 13) with $\tau = \tau_{\min} = 35 (h_0/h_{\text{init}})^5$ and needing $6\tau_{\min}$ to reach the point of bursting. Development of fluctuations to ruptures are shown beginning at three different points on the drainage curve. The time required for drainage to a given thickness is greater, but the time required for development of a fluctuation from that thickness to rupture is less, the smaller the thickness, so that the time required for rupture is relatively independent of the path followed.

to drain during the growth of the fluctuation. It is easily found that the critical thickness h_{crit} is equal to $\sqrt{5/7} \times h_m = 0.845h_m$. With this relation and calculating h_m from eq 18, 17, 19, and 16 we find

$$h_{\text{crit}} = 0.845h_m = 0.845\left(\frac{A^2 r^2}{320\pi^2 f\gamma P}\right)^{1/7} = 0.267(A^2 r^2/f\gamma P)^{1/7} \qquad (20)$$

Recent results by Exerowa and Kolarov[13d] for the drainage of dilute solutions of isovaleric acid in 0.1 M KCl confirm the dependence of the critical thickness on the $^2/_7$ power of the radius (calculated $r^{0.286}$, found $r^{0.27}$).[18] From these same data considering that the pressure P is given by the capillary suction at the plateau border which was 482 dynes/cm^2 in these experiments and using $\gamma = 55.5$ dynes/cm, a value for $A = 1.5 \times 10^{-13}$ erg can be derived, which is on the low side, but still very reasonable.

Sonntag, who determined the critical thickness of water films between oil layers,[19] confirmed that the critical thickness was independent of the viscosity. He found no influence of the surface tension (varied between 4 and 16 dynes cm^{-1}), whereas eq 20 predicts a variation of h_{crit} with about 20%.

van der Waals constants A, calculated from eq 20, are usually somewhat low, or inversely the critical thickness as calculated is usually somewhat higher than the values found experimentally (cf. ref 12), but the differences are not too large.

It is therefore felt that the mechanism of spontaneous growth of fluctuations, as described here, may well be the most important mechanism for breaking of emulsions and foams in the absence of vibrations, contaminations by outside sources, or chemical reactions. If this is confirmed on further research, our understanding of the stability of emulsions and foams will be greatly advanced. It is also evident that the theory still requires a great deal of refinement and, in particular, the surface elasticity of the surfactant layer should be taken

(18) A. Vrij, Discussions Faraday Soc., 42, 60 (1966), discussion remark.
(19) H. Sonntag, ibid., 42, 60 (1966), discussion remark.

into account. Results of preliminary calculations show that even a very small surface elasticity ($\gg A/8\pi h_0{}^2$) is usually sufficient to make the surfaces behave as rigid. When surface elasticity is completely absent (no surfactant present), drainage and growth of fluctuations are greatly accelerated and bursting occurs starting at much thicker films. More definite calculations, including surface elasticity and diffusion of surfactant, are now made in a cooperation between our Laboratory and the Unilever Research Laboratory at Vlaardingen, Netherlands (Dr. M. van den Tempel, et al.).

Combined Action of Metal and Semiconductor Catalysts[1]

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Contribution from the Institute of Physical Chemistry, University of Munich, Munich, Germany. Received November 27, 1967

Abstract: The slow oxidation of methanol vapor in an oxygen stream has been investigated by chromatographic methods. Zinc oxide and silver are both catalysts of the reaction and differ in specificity. A combination of both catalyst powders shows a surprisingly superior action. The result is compared with other similar observations and is interpreted on the basis of boundary layer theory. The idea of electron transfer from the metal into the semiconductor is confirmed by conductivity measurements.

In previous work it has been shown that the activity of a metal catalyst can be modified by supporting the catalyst on a semiconductor.[2-4] More intensive effects have been achieved by spreading a semiconductor catalyst on a metal carrier.[5-7] From this point of view, zinc oxide as catalyst has been used for the oxidation of methanol in the temperature range between 100 and 400°.

The first experiments were made with zinc powder which, as is well known, consists of zinc particles covered by zinc oxide. A dynamic reactor was used as described by Ettre and Brenner[8] and by Menold.[9] The products of the reaction were analyzed on a Perkin-Elmer gas chromatograph, Model 116 E. To achieve high resolution, the method of switching between three different columns was applied (column R, polypropylene glycol on Celite; column JoCe, silica gel; and column I, molecular sieve, 5 Å from Perkin-Elmer).

In these experiments no difference could be observed between the zinc powder described and pure zinc oxide. Therefore we sought to determine whether silver, already proved as an active carrier, would exert an effect. A mixture was prepared from fine silver powder and fine zinc oxide powder, pressed into pellets, and powdered once more. This mixture, designated below as "Ag·ZnO," was placed in a boat in the reactor at a methanol partial pressure of 100 torr in an air stream. In the temperature range between 100 and 150° an explosion was observed, although, over the single catalysts zinc

(1) Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 13, 1967.
(2) G.-M. Schwab, *Angew. Chem.*, **73**, 399 (1961).
(3) G.-M. Schwab, J. Block, and D. Schultze, *ibid.*, **71**, 101 (1959).
(4) G.-M. Schwab and G. Mutzbauer, *Z. Physik. Chem.* (Frankfurt), **32**, 367 (1962).
(5) G.-M. Schwab and R. Siegert, *ibid.*, **50**, 191 (1966).
(6) G.-M. Schwab and H. Derleth, *ibid.*, **53**, 1 (1967).
(7) G.-M. Schwab, F. Steinbach, H. Noller, and M. Venugopalan, *Z. Naturforsch.*, **19a**, 445 (1964); *Nature*, **193**, 774 (1962); see also F. Steinbach, *Angew. Chem.*, **79**, 1019 (1967); *Nature*, **193**, 774 (1962).
(8) L. S. Ettre and N. Brenner, *J. Chromatog.*, **3**, 524 (1960).
(9) R. Menold, *Chem.-Ing. Tech.*, **32**, 801 (1960).

oxide and silver, oxidation starts only at temperatures as high as 250°.

The lower explosion limit of a methanol–air mixture is 6% by volume of methanol. Therefore, further experiments were carried out with a methanol partial pressure of 38 torr corresponding to 5.3 vol %. It is admitted that now, in view of the smaller yield, reaction products formed in small amounts can no longer be analyzed.

The results of the measurements are represented by Figures 1–4. The partial pressures of the reaction products CO_2, H_2O, H_2, and CO have been plotted as a function of the reaction temperature for the following catalysts: ZnO, 0.8 g of ZnO powder; Ag, 0.8 g of Ag powder; Ag·ZnO, equal amounts by weight mixed as above, total weight 0.8 g; Ag + ZnO, 0.4 g of ZnO powder and 0.4 g of Ag powder in two separate boats. Interchange of the relative positions of silver and zinc oxide in the gas stream gave identical results, indicating full longitudinal diffusion mixing.

The following results can be seen in the figures. Carbon dioxide is formed by all the catalysts used, water vapor is formed in all cases except with pure zinc oxide, hydrogen is not formed by silver and by the mixed catalyst, and carbon monoxide is formed only by zinc oxide and only intermediately. It appears that the presence of silver generally suppresses the formation of carbon monoxide; as for hydrogen as a product, silver alone does not give it and it even suppresses its final occurrence with the mixed catalyst.

The most striking fact, however, is that the mixed catalyst gives an extremely high yield in water vapor and carbon dioxide as low as the temperature range between 130 and 200°, in contradistinction to the single catalysts which are not active below 250° and even higher than Ag + ZnO which shows a synergistic effect in Figures 1 and 2.

Methyl formate, formaldehyde, and formic acid could not be traced in any case, probably for the reason