Tests seem to indicate that the contamination of the interface solid–vapor with the solute can often be made so small that $\gamma_s = \gamma_{s'}$ so in this case (1) − (2) gives $\gamma_{sl} - \gamma_{sl'} = F = \gamma_l \cos \theta_1 - \gamma_{l'} \cos \theta_2$ where the quantities in the right hand term can be measured. Now since

$$\left(\frac{\partial F}{\partial a}\right)_T = -\left(\frac{\partial \gamma'}{\partial a}\right)_T$$

where a is the activity of the solute, the adsorption may be obtained by the equation of Gibbs. This gives the area a per molecule adsorbed. The area A, which refers to the total number of molecules of solute in the monolayer, is slightly less than a, since some molecules are already present.

Of the measurements made thus far, only those in which butyl alcohol is a solute are cited here. The relations are given in Fig. 1 for films of this substance at (1) the water–vapor, (2) the water–solid paraffin, and (3) the water–stibnite interface.

For a film which acts as a perfect gas $FA/kT = 1$. Since at a film pressure of 40 dynes per cm. the pressure per sq. cm. is of the order of 700 atmospheres, high pressures are involved.

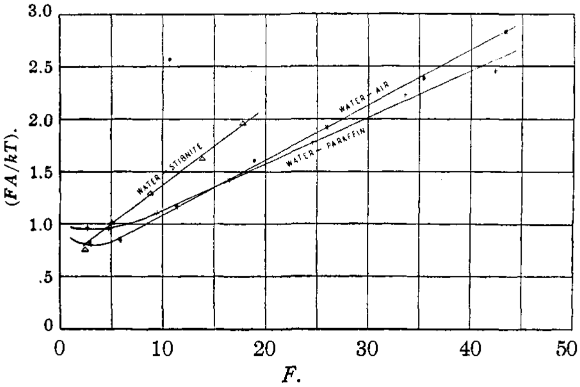

Fig. 1.—Pressure-area relations of films at the solid-liquid interface.

Obviously from Fig. 1 the films are gaseous at low pressures. If solid or liquid at high pressures there should be a vertical drop in the curve for the transition region, and then an ascending straight line which extrapolates through the origin. Thus, even though these monolayers are adsorbed on a solid they are nevertheless gaseous. Acetic acid films between water and solid paraffin are also gaseous.

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Received April 22, 1938

STEROLS. XXXIV. THE ISOLATION OF HEXAHYDRO-OESTRADIOLS FROM HUMAN NON-PREGNANCY URINE

Sir:

While no investigations of the steroid content of non-pregnant female urine have been reported, it is known that very little oestrogenic material is present [Loewe and Lange, *Klin. Wochschr.*, **5**, 1038 (1926)]. We have now isolated from this source, after removal of a small amount of pregnanediol, two isomeric diols, $C_{18}H_{30}O_2$, the more insoluble melting at 242° and giving a good depression in melting point with pregnanediol and *allo*-pregnanediol. *Anal.* Calcd. for $C_{18}H_{30}O_2$: C, 77.6; H, 10.9. Found: C, 77.4; H, 10.8. The diacetate melted at 160°. *Anal.* Calcd. for $C_{22}H_{34}O_4$: C, 72.9; H, 9.5. Found: C, 73.2; H, 9.7. The second isomer melted at 204°. *Anal.* Calcd. for $C_{18}H_{30}O_2$: C, 77.6; H, 10.9. Found: C, 77.6; H, 10.8. It gave a diacetate melting at 160°, which gave a good depression in melting point with the first diacetate. *Anal.* Calcd. for $C_{22}H_{34}O_4$: C, 72.9; H, 9.5. Found: C, 72.8; H, 9.5. These compounds are present in non-pregnancy human urine, but they do not appear present in pregnancy urine for their easy mode of isolation makes it extremely unlikely that they would have been overlooked in our extensive investigation of the steroid content of this material. Both diols are hexahydro-oestradiols, for they yield equilenin on heating with platinum black. Furthermore, the less abundant lower melting and more soluble isomer is identical with a diol obtained by the catalytic hydrogenation of oestrone according to the method of Dirscherl [*Z. physiol. Chem.*, **239**, 53 (1936)]. This latter diol yields a diketone m. p. 148° (*Anal.* Calcd. for $C_{18}H_{26}O_2$: C, 78.8; H, 9.5. Found: C, 79.0; H, 9.6), different from the diketone m. p. 124° (*Anal.* Calcd. for $C_{18}H_{26}O_2$: C, 78.8; H, 9.5. Found: C, 79.2; H, 9.8) obtained from the diol, m. p. 242°, so the two carbinols must be stereoisomers, differing at least in regard to the configuration at C-5 or C-10. Neither diol is precipitated by digitonin, and both are saturated to bromine.

Since these diols, which evidently arise from the biochemical reduction of oestrone, are not present in pregnancy urine, their presence in non-pregnancy urine indicates that they are not merely enzymatic reduction products, but are associated with the use of oestrone when it functions as a hormone, arising from the latter by reductive processes as do the various carbinols and ketones, from progesterone and androstenedione [Marker, THIS JOURNAL, in press (1938)]. The details of this work will be published in a forthcoming issue of THIS JOURNAL.

We wish to thank Dr. Oliver Kamm and Parke, Davis and Company for their generous help and assistance in various phases of this work.

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RECEIVED MAY 21, 1938

KINETICS OF THE EXPLOSIVE REACTION BETWEEN HYDROGEN AND OXYGEN SENSITIZED BY NITROGEN PEROXIDE

Sir:

In a recent paper, von Elbe and Lewis [THIS JOURNAL, **59,** 2022 (1937)] propose a scheme of reactions for the above process, having concluded that "the evidence rules out a mechanism based on oxygen atoms." In arriving at this conclusion these authors did not discuss the relevant work of Norrish and Griffiths [*Proc. Roy. Soc.* (London), **A139,** 147 (1933)], and of Foord and Norrish [*ibid.*, **A152,** 196 (1935)] in which new evidence based on the study of the induction period and the effect of irradiation by light is presented.

Without dogmatizing about the precise nature of the chain mechanism we concluded in the light of the new facts that a mechanism involving oxygen atoms is by no means excluded. Such a scheme is indeed capable of giving a fair description of the facts and no other scheme has yet been advanced which has been shown to take our new facts into consideration.

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R. J. W. NORRISH

RECEIVED APRIL 20, 1938

EFFECT OF X-RAYS ON SURFACE POTENTIALS OF MULTILAYERS

Sir:

Porter and Wyman [THIS JOURNAL, **60,** 1083 (1938)] have reported that stearate X- or Y-films on grounded metal plates acquire negative potentials when exposed to x-rays.

We have produced charges on both X- and Y-multilayers in many different ways, measuring the potentials by the vibrating-plate method and with a polonium–air electrode. This work suggests that the ionized air and the electric field near the x-ray tube are responsible for the charge on the film.

We confirm Porter and Wyman's observation that a self-rectifying x-ray tube in air, operating on 60 kv., a. c., charges the films a few volts negatively even when either tube terminal is grounded. However, if an oil-immersed shock-proof x-ray tube is used or if the metal plate is enclosed in a thin aluminum box, a 10-minute exposure, with the same x-ray dosage (28 roentgens), has no effect on the film potential.

Multilayer films exposed to x-rays from a tube in air, operated on 60 kv., d. c., acquire large potentials (10 volts on only 21 layers). The film becomes positively charged if it is at cathode potential and negatively charged if at anode potential, regardless of which terminal is grounded.

When there are high voltage terminals in air, the ionization of the air by x-rays permits a current to flow which can charge the film. We have found that with 60 kv., a. c., applied to a tube in air with its cathode cold so that no x-rays are generated, the films do not become charged. If, however, a pointed wire is attached to the anode terminal so that a corona discharge occurs, the plate becomes negatively charged although there are no x-rays.

A charged film on a grounded plate can be discharged in a few minutes if a grounded polonium electrode is brought close to its surface. Undoubtedly x-rays would discharge a charged film in an aluminum box if x-ray dosages of more than 100 roentgen units were used.

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RECEIVED MAY 24, 1938

THE RELATION BETWEEN RATES OF GENERAL BASIC CATALYSIS IN DIFFERENT REACTIONS

Sir:

It is a well-known characteristic of reactions which are susceptible to general catalysis by bases in the Brönsted sense that the logarithmic plot of catalytic constants k_B against corresponding basic association constants K_B yields several straight lines corresponding to the various charge types, rather than one single straight line.[1] Furthermore, certain substitutions on or near the re-

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[1] Kilpatrick and Kilpatrick, *Chem. Rev.*, **10,** 213 (1932); Pedersen, *J. Phys. Chem.*, **38,** 581 (1934).