g. of ferric oxide, gave results with an average deviation of 4.5 parts per thousand.

Similar analyses of solutions containing simultaneously 0.1 to 0.2 g. of nickel, zinc, cobalt, manganese, copper and cadmium oxides and of solutions containing simultaneously 0.05 to 0.1 g. of potassium, aluminum, magnesium, calcium, beryllium, lanthanum, erbium and neodymium oxides were also conducted with a similar degree of concordance.

Chromium.—Complete separation of iron from chromium as dichromate was obtained by one reprecipitation. The precipitate was washed only with the dilute hydrochloric acid, then dissolved in the original beaker in 20 cc. of 1:1 hydrochloric acid. After preparing the solution as described, the iron was precipitated by adding 0.60 g. of reagent dissolved in 100 cc. of hot water.

Employing 0.0509 g. of ferric oxide and approximately equal amounts of chromic oxide, three determinations gave 0.0508, 0.0510, and 0.0508 g. of ferric oxide.

Thallium.—The strong tendency for thallic salts to hydrolyze necessitated as a first wash solution a saturated solution of the reagent in 1% hydrochloric acid. This was followed by the usual one with warm water to remove chloride.

Five determinations involving 0.0509 g. of ferric oxide and amounts of thallic oxide from 0.04–0.20 g. gave an average value of 0.0510 g.

Vanadium.—Separations of iron from vanadium when in the vanadate state gave no difficulty. With approximately 0.05 g. of ferric oxide in the presence of 0.01–0.02 g. of vanadium pentoxide, nine determinations gave results with an average deviation of 2.5 parts per thousand.

Determination of Iron in Monel Metal and German Silver.—A monel metal containing 35.48% copper, 57.36% nickel, 0.10% manganese, 0.71% insoluble, and 6.28% iron was analyzed as already described. Employing one-gram samples, four determinations gave an average value of 6.32% iron. A German silver containing 55.99% copper, 20.15% nickel, 23.38% zinc, small % insoluble, and 0.11% iron was analyzed in a like manner. Three determinations, employing two-gram samples, gave an average value of 0.11% iron.

Interfering Elements and Radicals.—The precipitation of iron is prevented by the presence of radicals with which it forms complexes such as fluoride, phosphate, tartrate, and citrate.

Iron cannot be determined in the presence of the following ions of the fourth periodic group: zirconium, tin, titanium and thorium nor in the presence of uranium and cerium. Since the precipitation is made in hot solution, hydrogen peroxide could not be used satisfactorily to hold up titanium. Iron failed to precipitate completely in cold solutions.

Further investigation of the separation of these elements with this reagent and with other substituted phenylarsonic acids is in progress.

Summary

1. A new gravimetric method has been described for the determination of iron in which it is precipitated with *p*-*n*-butylphenylarsonic acid.

2. By this method the direct determination of iron is possible in the presence of a large number of elements with which it is commonly associated.

3. Iron cannot be determined by this method in the presence of zirconium, tin, titanium, thorium, uranium and cerium or in the presence of radicals with which it forms complexes such as fluoride, phosphate, tartrate and citrate.

STATE COLLEGE, PA. RECEIVED FEBRUARY 26, 1934

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

The Calculation of Heterogeneous Reaction Rates

BY ROBERT E. BURK

Attempts to correlate catalytic reaction rates on surfaces with kinetic estimates of what they should be, have long been frustrated[1] because an adequate knowledge of the number of molecules adsorbed in the particular way required for reaction could not be arrived at.

However, J. B. Taylor and I. Langmuir[2] through a study of cesium films adsorbed on tungsten have developed a remarkable knowledge of a tungsten surface which has been etched by heating to a high temperature in a high vacuum. Langmuir had found in earlier work[3] that a tungsten surface which had been heated to such high temperature that some evaporation had occurred, consisted exclusively of dodecahedral faces, and that the extent of the total developed surface does not increase as the size of the faces increases.

Taylor and Langmuir were then able to show that with respect to cesium adsorption this surface may be divided into two portions, one portion A representing 0.5% of the surface is able to hold cesium far more strongly than the rest. This

---

[1] Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," 3d ed., Oxford, 1933, p. 357.

[2] J. B. Taylor and I. Langmuir, *Phys. Rev.*, **44**, 423 (1933).

[3] Langmuir, *ibid.*, **22**, 374 (1923).

portion evidently represents crystal edges while the portion B which is 99.5% of the surface evidently represents the crystal faces. The whole surface was thought to be 1.347 times the apparent surface. Acceptance of these values therefore allows an estimate of the extent of each type of surface to be made.

When the writer was a National Research Fellow in Cornell University he carried out some kinetic investigations[4] on the thermal decomposition of ammonia on pure tungsten filaments obtained from the Eisler Engineering Co. Wire A was aged for one hour at about 2400°K. in a vacuum at least as good as 0.0001 mm. Wire C was aged under about the same conditions although the time was not recorded in this case. These aging temperatures according to Langmuir[5] are sufficient to produce substantial evaporation and therefore should develop the dodecahedral structure.

At the concentrations used in this work (100 mm. initial concentration of ammonia) the surface reaction is almost zero order[6] over the half-life period, but at the temperatures used (1266 to 1481°K.) is in reality unimolecular.[6b,7] This circumstance shows that reaction occurs when properly adsorbed ammonia molecules receive energy from the surface, and not directly by collision from the gas phase nor by collision with each other on the surface. It also shows that the rate of adsorption cannot influence the observed rate of reaction, nor can the products of reaction under the conditions prevailing. The active surface must be substantially completely covered with ammonia at all times. The observed energy of activation is therefore approximately the correct one,[8] except for errors in experimental technique. It was 47,000 calories on wire A and 48,000 calories on wire C and compares with 45,250 to 49,750 obtained by Kunsman. The precise method used by Kunsman in aging his filament was not stated, the highest temperature mentioned by him for glowing being, however, 1600°. He noted, as did the present writer, that glowing the filament deactivated it for decomposing ammonia. In our work however the wires attained a steady state of activity after a few decomposition experiments, which indicated to us that the underlying structure of tungsten atoms was not changing. If as is likely a film (nitride?) was forming on the tungsten surface during this period of activation, it is in all probability not more than one molecule thick and therefore would not blur Langmuir's picture of the surface structure nor the following calculation.

The volume of our bulb was approximately 470 cc. In it the rate of decomposition of ammonia was determined from measurements of pressure rise and time, the static method being employed. The bulb was immersed in ice. Both synthetic ammonia and that made from Kahlbaum pure ammonium chloride gave the same results. It was stored in a bulb containing a drying agent. With some preparations possible traces of oxygen were removed by heating a platinum filament in the storage bulb until incipient decomposition of the ammonia occurred. The various modes of preparing the ammonia were not found to affect the results. The ammonia was introduced into the highly evacuated reaction vessel. The temperature was determined from the resistance of the wire. The resistance at 0° varied, being as much as 10% higher after heating in ammonia as compared with the value after heating *in vacuo*. On the latter basis the resistance at 0° of wire A was 2.019 ohms compared with 2.015 computed from Forsythe and Worthing's[9] values for the resistivity of aged tungsten. Our filament was about 7.9 cm. in length and about 0.005 cm. in diameter. The *in vacuo* value of the resistance was chosen on the ground that the high temperature resistance probably also represented the wire in a degassed condition. Corrections were made for the resistance of the leads and for end losses.[10] It should be pointed out that the tendency of a thin filament to overheat at points of small diameter is counteracted in this case by the endothermic nature of the reaction. In spite of these precautions the writer is unable to estimate the accuracy for the absolute temperatures although the relative temperatures should be quite good.

Pressure was measured by means of a small bore mercury manometer whose volume was less than one-quarter of one per cent. ot that of the bulb.

---

(4) Burk, *Proc. Nat. Acad. Sci.*, **14**, 601 (1928).

(5) Langmuir, *Phys. Rev.*, **2**, 340 (1913).

(6) (a) See also Hinshelwood and Burk, *J. Chem. Soc.*, **127**, 1105 (1925); (b) Kunsman, THIS JOURNAL, **50**, 2103 (1928).

(7) Hailes, *Trans. Faraday Soc.*, **27**, 601 (1931). The results of Frankenburger and Hodler, *ibid.*, **28**, 229 (1932), are for conditions so different that they hardly enter this discussion. Schwab, *Z. physik. Chem.*, **128**, 175 (1927).

(8) Hinshelwood, *loc. cit.*, p. 355.

(9) Forsythe and Worthing, *Astrophys. J.*, **61**, 146 (1925).

(10) Langmuir's formula $\Delta V = 0.00026\ (T - 1.3\ T_0)$ was used. T is the temperature of the central portion of the filament and T_0 is the temperature of the leads (*Trans. Faraday Soc.*, **17**, 634 (1922)).

The following data were obtained with the wires sufficiently seasoned to give reproducible results, which means that the half lives can be reproduced within about 10% and less than this in successive experiments at the same temperature.

TABLE I

Expt.	Half life, sec.	T, °K.	E, calories
20 A	140	1403	47,000
18 A	730	1279	
21 A	58	1481	
10 C	135	1435	48,000
11 C	605	1306	
12 C	231	1385	
14 C	1285	1266	
16 C	387	1349	

From Lindemann's formula[11] one obtains the value 5.899 × 10^{12} for the vibration frequency V of the tungsten atoms in metallic tungsten.

If we assume that reaction occurs when an ammonia molecule adsorbed in such a way as to have a unimolecular energy of activation of E calories receives an impact from an underlying tungsten atom which possesses E calories, the mean life of such a molecule (with respect to reaction not adsorption) would be given[12] by $(1/V)e^{E/RT}$. This gives the value $\tau_{\text{calcd.}}$ in the following table.

The columns in Table II marked A or B mean that the calculations were performed on the basis of the reaction occurring exclusively on the surface fraction A or B, respectively. A positive discrepancy factor signifies that the calculated mean life is too small. The constancy of the discrepancy factors shows the extent to which the points on the heat of activation curve (not shown) lie on a straight line of slope E. It is to be noted that factors which have been neglected in this calculation such as the probability that each vibration with the energy E will not communicate its energy to the adsorbed ammonia molecule will make the discrepancy factor more negative. Furthermore, since the reaction is almost but not quite zero order and since the energy of activation tends to fall at higher temperatures[14] the energy of activation used in the present calculations is probably somewhat low. A choice of a higher value would also make the discrepancy factor more negative. The value would have to be 52,300 calories to remove the discrepancy factor of 7.8.

The discrepancy factor of 7.8 could also be removed by a temperature error of 132° (from 1300°K.). This is probably greater than the real error.

TABLE II

Expt.	$e^{-E/RT}$	τ(observed) A	τ(observed) B	$\tau_{\text{calculated}}$	Discrepancy factor A	Discrepancy factor B
20 A	$10^{-7.33}$	1.4×10^{-7}	2.78×10^{-5}	3.55×10^{-6}	−25.3	+7.84
18 A	$10^{-8.04}$	7.27×10^{-7}	1.45×10^{-4}	1.82×10^{-5}	−25.0	+7.97
21 A	$10^{-7.11}$	5.78×10^{-8}	1.15×10^{-5}	1.5×10^{-6}	−25.2	+7.89
10 C	$10^{-7.32}$	1.34×10^{-7}	2.67×10^{-5}	3.5×10^{-6}	−26.7	+7.72
11 C	$10^{-8.04}$	6.03×10^{-7}	1.2×10^{-4}	1.82×10^{-5}	−30.2	+6.58
12 C	$10^{-7.425}$	2.3×10^{-7}	4.57×10^{-5}	6.34×10^{-6}	−27.5	+7.20
14 C	$10^{-8.29}$	1.28×10^{-6}	2.55×10^{-4}	3.27×10^{-5}	−25.6	+7.78
16 C	$10^{-7.78}$	3.86×10^{-7}	7.68×10^{-5}	1.01×10^{-5}	−26.2	+7.60

Using the value[13] 1 × 10^{-15} sq. cm. for the area occupied by an adsorbed ammonia molecule, the A fraction of our surface will accommodate about 8.35 × 10^{11} molecules and the B fraction about 1.66 × 10^{14} molecules. The bulb contained at the beginning of each experiment about 1.68 × 10^{21} molecules.

Various workers now agree that activating adsorption of molecules probably requires in general more than one surface atom.[15] This would tend to make our discrepancy factor more positive by possibly two or three times, but this could probably be absorbed by the factor representing restraint in energy transfer.

Thus even when other factors are considered the B surface leads to a rate closer to the observed

---

(11) Nernst, "Theoretical Chemistry," The Macmillan Co., New York, 1923, p. 282.

(12) While one is accustomed to associate unimolecular reactions with a time lag after activation, such a time lag is probably a minor factor in the present case, the mechanism being more in the nature of a bimolecular reaction between surface tungsten atoms and adsorbed ammonia because of direct communication of energy from the former to a particular "stretched" bond of the latter. Such a process would of course be "unimolecular" with respect to ammonia.

(13) Frankenburger and Hodler, *Trans. Faraday Soc.*, **28**, 236 (1932); Jona, *Physik. Z.*, **20**, 14 (1919); Grimm, *Z. Elektrochem.*, **31**, 474 (1925).

(14) Kunsman, *loc. cit.* It should be mentioned that in Kunsman's work filaments of W, Mo and Ni were used in the same bulb. If these were properly aged by heating *in vacuo*, mutual contamination of the surfaces would result which (Burk, *loc. cit.*) would affect the catalytic properties of the wires and in particular may result in lowered energies of activation.

(15) Burk, *J. Phys. Chem.*, **30**, 1134 (1926); Balandin, *Z. physik. Chem.*, **132**, 289 (1929); Polanyi, *Z. Elektrochem.*, **35**, 9 (1929); Sherman and Eyring, THIS JOURNAL, **54**, 2661 (1932).

than the A surface, and they may very possibly make the calculated rate on the B surface equal to the observed rate.

Summary

These calculations indicate that the high temperature thermal decomposition of ammonia on "aged" tungsten occurs uniformly on its dodecahedral faces and at such a rate that almost every vibration of underlying tungsten atoms with the energy of activation leads to reaction. The obvious factors which have been neglected in the calculation affect it in a way which supports this conclusion.

CLEVELAND, OHIO RECEIVED FEBRUARY 26, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Solubilities of Some Organic Oxygen Compounds in Sulfuric Acid–Water Mixtures

BY LOUIS P. HAMMETT AND RAY P. CHAPMAN

The fact that most organic oxygen compounds are very soluble in concentrated sulfuric acid, and that some, notably ethyl ether and cellulose, possess a largely increased solubility in very concentrated aqueous hydrochloric acid, is reasonably familiar. The phenomenon has indeed received technical application in such processes as the purification of anthraquinone,[1] in the preparation of parchment paper,[2] and probably in the zinc chloride process for vulcanized fiber.[3] The eminently reasonable hypothesis that the increased solubility results from salt formation between the basic oxygen compound and the strong acid has been suggested for particular groups of compounds by a number of investigators.[4] This hypothesis has especial interest because of the possible application of the solubility method to the determination of the strength of very weak bases, and is open to quantitative investigation now that there is available a series of indicators by means of which a measure of acidity may be obtained over the whole range of sulfuric acid–water mixtures.[4e,5] We have therefore undertaken the determination of the solubility of some typical oxygen compounds in sulfuric acid–water mixtures of a much wider range of compositions than was accessible to the analytical methods used by previous workers.

Methods and Materials

All measurements were at 25 ± 0.02°.

Sulfuric acid–water mixtures of the desired concentrations were standardized by titration, using Bureau of Standards benzoic acid or potassium acid phthalate as ultimate standards. These solutions together with an excess of the organic solute were rotated in a water thermostat. The containers were bottles with accurately ground stoppers, which were protected by a paraffin seal and by rubber tubing. It was found in a number of cases that no further increase in solubility took place after twenty hours, and this period of rotation was adopted as a minimum. In the case of the solid solutes, the saturated solution was filtered without removal from the thermostat through an immersion filter of the fritted glass type. With nitrobenzene, the saturated aqueous layer was separated carefully.

In the experiments on benzoic acid and on phenylacetic acid the concentration of the saturated solutions was determined by the continuous extraction method previously described by us.[6] Experiments on known amounts of phenylacetic acid showed the method to have the same precision (about 1%) with this acid as with benzoic. The concentration of the nitro compounds was determined by reduction with titanous sulfate using essentially the method of Callan and Henderson,[7] which we have found to be capable of a precision of about 1% by experiments on known amounts of the three compounds in question. The concentration of benzoyldiphenyl was determined by colorimetric comparison of the saturated solution with a solution of known concentration of the compound in sulfuric acid of the same concentration as was used in the preparation of the saturated solution.

Experiments with indicators showed that not even at the highest acid concentrations studied was the solubility of benzoic acid sufficiently large to have a measurable effect upon the acidity function, H_0,[5] of the sulfuric acid–water solution.

In the analysis of the wet solid phase, the organic acid was determined by the same method as was used with the solutions, and the sulfuric acid was determined either by difference from a determination of total acidity or by titration of the residual acid in the extractor after the removal of the organic acid.

---

(1) Ullmann, "Enz. d. techn. Chem.," 2d ed., Vol. I, p. 200.

(2) Ullmann, *ibid.*, Vol. VIII, p. 290.

(3) Frey and Elöd, *Ber.*, **64B**, 2556 (1931).

(4) (a) Jüttner, *Z. physik. Chem.*, **38**, 56 (1901); (b) Sackur, *Ber.*, 35, 1242 (1902); (c) Knox and Richards, *J. Chem. Soc.*, **115**, 508, 850 (1919); (d) Kendall and Andrews, THIS JOURNAL, **43**, 1545 (1921); (e) Hammett, *Chem. Rev.*, **13**, 61 (1933).

(5) (a) Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932); (b) Hammett and Paul, *ibid.*, **56**, 827 (1934).

(6) Chapman and Hammett, *Ind. Eng. Chem.*, *Anal. Ed.*, **5**, 346 (1933).

(7) Callan and Henderson, *J. Soc. Chem. Ind.*, **41**, 157T (1922).