[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Kinetics of the Heterogeneous Ammoniation of Urea and Thiourea[1]

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Pressure–composition isotherms for the systems urea–ammonia and thiourea–ammonia at −35.0° provide evidence for the formation of only the corresponding 1-ammoniates. On the basis of rate data for temperatures of −35.0 and 0.0°, it is shown that for conditioned solid samples these solid–gas ammoniation reactions are essentially independent of the source or state of aggregation of the solid, first order with respect to ammonia pressure, zero order with respect to the initial weight of solid (for small sample weights), and apparently zero order with respect to surface coverage. In the latter case, a direct correlation exists between the surface coverage and the retardation of the ammoniation reaction. The "true energy of activation" for these ammoniation reactions is 0.5–1.0 kcal./mole. The dissociation pressures of the 1-ammoniates of urea and thiourea at −35.0° are 104 and 33 mm., respectively.

Although several aspects of heterogeneous ammoniation involved in the attainment of thermodynamic equilibrium were investigated previously in conjunction with pressure–composition isotherms for the ammonium halides,[2] the effect of the marked increase in the volume of certain compounds during their initial ammoniation was not considered at that time. While the initial ammoniation of ammonium fluoride and ammonium chloride is first order with respect to the salt, it was observed that the subsequent rate of reammoniation of these salts was much greater than the initial rate under comparable conditions and that the order of the reaction was changed. The present study summarizes similar additional observations concerned with the heterogeneous ammoniation of urea and thiourea.

Experimental

The nature of the quartz helix balance and the techniques employed in the establishment of pressure–composition isotherms are described elsewhere.[2] All chemicals used were reagent grade.

The *initial* ammoniation of 0.1600 g. of urea at 470 mm. and −35.0° and of 0.1205 g. of thiourea at 900 mm. and 0.0° is shown in Fig. 1 as a first-order reaction with respect to the solid compound ammoniated. The pressure–composition isotherms for the systems urea–ammonia and thiourea–ammonia at −35.0° are included in Fig. 2; the phases coexistent at equilibrium are listed in Table I which includes also the data of Janecke, *et al.*, relative to metastable systems involving the 3-ammoniate of thiourea.[3,4]

TABLE I

COMPOSITION OF PHASES AT EQUILIBRIUM

Curve	Phases
AB	U(s),^{a} U·NH_3(s), NH_3(g)
BC	U·NH_3 (s), NH_3(g)
CD	U·NH_3(s), satd. soln., NH_3(g)
EF	T(s),^{b} T·NH_3(s), NH_3(g)
FG	T·NH_3(s), NH_3(g)
GH	T·NH_3(s), satd. soln., NH_3(g)
HH′	Supersatd. soln., NH_3(g)^c
HI	Dil. soln., NH_3(g)
JK	T·NH_3(s), T·3NH_3(s), NH_3(g)^d
KL	T·3NH_3(s), NH_3(g)^d
LM	T·3NH_3(s), satd. soln., NH_3(g)^d

[a] U = urea. [b] T = thiourea. [c] Metastable. [d] Data of Janecke, *et al.*[3]

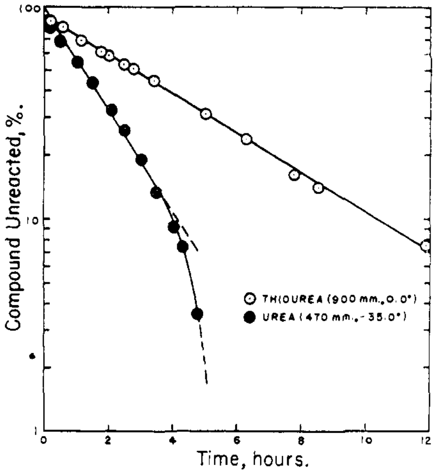

Fig. 1.—First-order rate plots for the initial ammoniation of urea and thiourea.

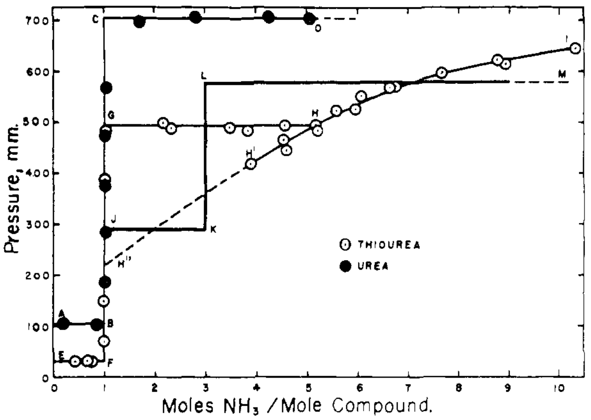

Fig. 2.—Pressure–composition isotherms at −35.0° for the systems urea–ammonia and thiourea–ammonia.

The procedure for conditioning the samples consisted of repeated ammoniation and deammoniation at the temperature at which the kinetic studies were to be made. For example, after the initial ammoniation of urea at −35.0° and 470 mm. (Fig. 1), the cyclic process of ammoniation, and deammoniation (at pressures of the order of a few millimeters), was repeated until no further change was evident in the rate of ammoniation at 470 mm. (see corresponding curve in Fig. 3). For subsequent rate measurements, the ammoniation was begun within ten minutes after deammoniation was complete. In order to ensure reproducibility of the systems under investigation, such factors as time, methods of deammoniation, temperature, source of materials ammoniated and thickness of the solid layer were studied in the light of their possible effects upon the ammoniation reaction. It was concluded that the conditioning process resulted in solids having kinetic properties that were strictly reproducible. Factors that measurably in-

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[1] This work was supported in part by the U. S. Navy Bureau of Ordnance, Contract N123s-67363, Task Order 2.

[2] G. W. Watt and W. R. McBride, THIS JOURNAL, **77**, 1317 (1955).

[3] E. Janecke and A. Hoffmann, *Z. Elektrochem.*, **38**, 880 (1932).

[4] E. Janecke and E. Rahlfs, *ibid.*, **36**, 648 (1930).

fluence the rate process are temperature and certain phase changes. The effect of temperature in the case of ammonium sulfate was measurable when the temperature of the conditioned sample was changed from −35.0° to room temperature for a period of 12 hr. A major limitation, however, is that the condensed phases must be limited to solids: the formation of a liquid phase, the existence of which may be only transitory, may disrupt the kinetics and even the conditioning process. For this reason it was important to select systems in which liquid phases could be avoided or eliminated. Compounds such as urea, thiourea, ammonium chloride,[2] ammonium fluoride[2] and ammonium sulfate[5] were found to be suitable from this point of view.

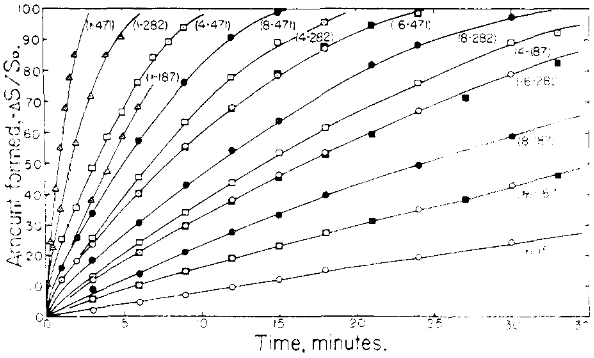

Fig. 3.—Rate of ammoniation of conditioned samples of urea at −35.0°.

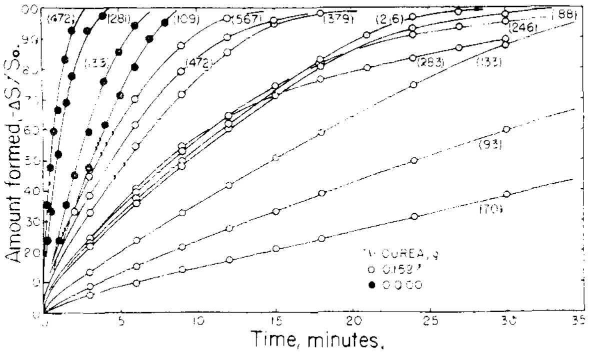

Fig. 4.—Rate of ammoniation of conditioned samples of thiourea at −35.0°.

Data relating to the ammoniation of conditioned samples of urea and thiourea at constant pressure are presented in Figs. 3 and 4, respectively. Data for the deammoniation of urea at constant pressure are given in Fig. 5. The data given in Figs. 2–5, inclusive, correspond to a temperature of −35.0° and are plotted as $\pm\Delta S/S_0$ (*i.e.*, the change in the amount of unammoniated solid divided by the initial amount) *vs.* time. A curve labeled, for example, 16–471 denotes 0.1600 g. of solid ammoniated at 471 mm.; only the pressure is specified in Fig. 4 since only two sample weights are involved.

Discussion

For a two-component system, the reversible ammoniation of a solid, S, to form a solid ammoniate, $S\cdot nNH_3$, by a solid-gas reaction

$$S(s) + nNH_3(g) \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} S\cdot nNH_3(s)$$

represents a type of case well suited for kinetic studies. Nevertheless, the evidence in the literature shows that these apparently simple systems are often quite complex and that information as to the attainment of thermodynamic equilibrium as a function of time is only fragmentary. For urea and thiourea, *n* in the above equation is 1, and is 3 for ammonium chloride and ammonium sulfate. The present and earlier work has shown that these solids may be prepared in a manner such that the kinetics of subsequent ammoniation is independent of the source of the compound ammoniated or its original state of aggregation. For urea or thiourea, the occurrence of the forward or reverse reaction depends only upon conditions that follow from the work of Janecke, *et al.*,[3,4] and the pressure–composition isotherms of Fig. 2.

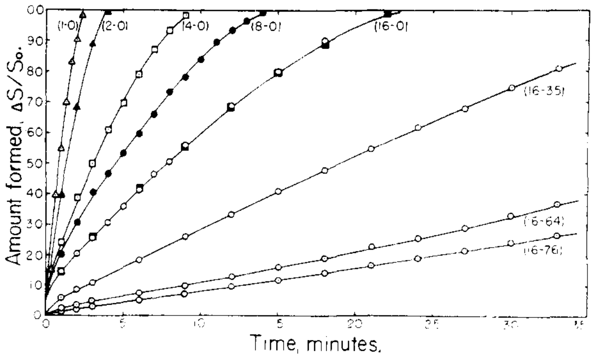

Fig. 5.—Rate of deammoniation of conditioned samples of urea at −35.0°.

As is shown by curve BC (Fig. 2—see also Table I), the 1-ammoniate of urea at −35.0° is stable from its dissociation pressure (104 mm.) up to approximately the condensation pressure of ammonia (703 mm.) at this temperature. By the phase rule, this corresponds to conditions under which only two phases are present and pressure is still a variable after the temperature is fixed. This is contrasted to curves AB and CD for which pressure becomes invariant owing to the formation of a third phase, *i.e.*, urea and a saturated solution of urea, respectively. At pressures below the dissociation pressure of the 1-ammoniate, the only stable solid phase is urea. Accordingly, at −35.0° the process of ammoniation may be investigated over the pressure range 104–703 mm. while deammoniation may be studied below 104 mm. For thiourea, the corresponding pressures are 33–495 mm. and 33 mm.

Three independent experiments at −35.0° failed to provide any evidence for the 3-ammoniate of thiourea reported by Janecke and Hoffmann.[3] Our data, however, are not necessarily in conflict with those of Janecke and Hoffmann since they do not suggest that the 3-ammoniate was prepared at −35.0° but only that once formed it behaved in the described manner at this temperature. Actually it would appear that they obtained this ammoniate from solution at a much lower temperature. They also state that over the temperature range −78 to −10° the 3-ammoniate is in equilibrium with the saturated solution (composition at −33.8°: 11.1 moles NH_3/mole NH_2CSNH_2). Accordingly, it can be deduced from Fig. 2 that curve HI represents at the same time a supersaturated solution with respect to the invariant pressure LM and a dilute solution with respect to the invariant pressure GH, while HH′ represents a solution supersaturated

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(5) C. M. Drew, H. W. Kruse, S. Skolnik and G. B. L. Smith, This Journal, **71**, 1494 (1949).

with respect to both invariant systems. This supersaturated solution finally crystallizes violently near H′ and forms the invariant system GH. On the other hand, the 1-ammoniate over the pressure range embraced by curve JG shows no tendency toward the formation of the 3-ammoniate and this stability can be explained only if the 3-ammoniate cannot be formed directly by a solid-gas reaction. Similar complications involving metastable systems have been encountered in the supersaturation of guanidinium chloride with respect to four invariant systems.[6]

The data of Fig. 3 show that the rate of ammoniation for conditioned samples of urea at −35.0° is independent of the source and state of aggregation of the urea initially used. Merck (reagent grade) and Mallinckrodt (analytical reagent grade) materials were used and the data (curves 16–471, 16–282, and 16–187) for the two samples are almost identical and well within experimental error. Similar results were obtained using large crystals of ammonium sulfate and the finely powdered salt precipitated from aqueous solution by addition of alcohol or ether. Figure 3 also shows that the rate of ammoniation is directly dependent upon the pressure (see curves cited above) and shows the extent to which rate is dependent upon the size sample employed (compare curves 16-187, 8-187, 4–187, 1-187, etc.).

The data relative to the heterogeneous ammoniation of *conditioned samples* of urea and thiourea may be treated in a manner analogous to that applicable to the adsorption of a gas on a solid surface. That is, all of the solid present behaves as surface available for ammoniate formation. Thus, the rate of ammoniation = $k_1p(1 - \theta)^n$ and the rate of deammoniation = $k_{-1}(\theta)^n$, where θ is defined as the fraction of the surface ammoniated and p is the ammonia pressure. At equilibrium

$$p = (k_{-1}/k_1)(\theta/1 - \theta)^n \qquad (1)$$

where $n = 0$ for the Gibbs isotherm[7] that is applicable in the present case. Thus it should be evident that for the Gibbs relationship the pressure-composition isotherms (Fig. 2) are a step function of the pressure rather than a continuous function, *i.e.*, the pressure p is a constant for any invariant system and may subsequently be designated as the dissociation pressure, p_0. Accordingly

$$p_0 = k_{-1}/k_1 \text{ or } k_{-1} = k_1p_0 \qquad (2)$$

and for this special case the rate constant for the reverse reaction may be determined from the dissociation pressure and the rate constant for the forward reaction (eq. 2). If k_1p_0 is substituted for k_{-1}, the net rate of ammoniation is

$$d(S{\cdot}NH_3)/dt = -d(S)/dt = k_1p(1 - \theta)^0 - k_1p_0(\theta)^0 \quad (3)$$

By an appropriate division or multiplication by $(\theta/1 - \theta)^0$, equation 3 reduces to equations 4 and 5, respectively. Thus for ammoniation

$$d(S{\cdot}NH_3)/dt = -d(S)/dt = k_1(1 - \theta)^0(p - p_0) \quad (4)$$

and for deammoniation

$$d(S{\cdot}NH_3)/dt = -d(S)/dt - k_1(\theta)^0(p - p_0) \quad (5)$$

These equations are of special interest since they account for both the case $p \geqq p_0$ in which ammoniation proceeds until $\theta = 1$ or $p = p_0$, and for the case $p \leqq p_0$ wherein deammoniation proceeds until $\theta = 0$ or $p = p_0$. Equations 4 and 5 may be simplified to

$$d(S{\cdot}NH_3)/dt = -d(S)/dt = k_1(p - p_0) \qquad (6)$$

Zawadzki and Bretsznajder[8] arrived at equation 6 through consideration of reactions of the type involved in the thermal dissociation of calcium carbonate, but they were unable to obtain experimental data compatible with this equation.

The data of Fig. 3 are plotted in Fig. 6 as log $[-d(S)/S_0dt]$ *vs.* log $(p - p_0)$, from which it is seen that the ammoniation process is first order with respect to ammonia pressure, $p - p_0$. This reaction is first order for the five series of experiments in which the initial amount of urea, S_0, was varied from 0.0100 to 0.1600 g. Since the method of plotting the data in Fig. 3 is equivalent to plotting the fraction of the solid surface ammoniated *vs.* time, the plot in Fig. 6 is thus the differential rate, $-d(S)/S_0dt$, which corresponds to the fraction of the surface ammoniated, θ/min. The data in Fig. 6 represent the differential rate for the case in which $\theta = 0.25$, and by inspection of the data of Fig. 3 corresponding particularly to lower pressures it may be concluded that this rate is nearly equal to the instantaneous rate.

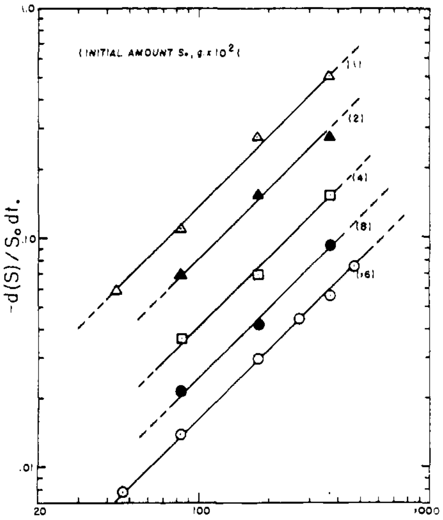

Fig. 6.—Differential rates of ammoniation of urea as a function of pressure.

Since equation 4 includes the term $(1 - \theta)$, it is desirable to determine the order of the reaction with respect to ammonia pressure at some arbitrarily chosen but constant ammoniation of the solid. If the assumptions made above are valid, the differential rate should be constant when the initial amount of urea is varied. From Fig. 6 this differential rate may be had almost by inspection since it is equal to $(-d(S)/S_0dt)(S_0)$. If $p - p_0$ is arbitrarily taken as 100 mm., $-d(S)/dt$ is proportional to 14.0, 16.2, 16.4, 19.4 and 25.6 as S_0 increases from 0.0100 to 0.1600 g. Thus for the smaller samples (thickness $\leqq$4 mm.), the ammoniation reaction is essentially zero order with respect to the initial

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(6) G. W. Watt and W. R. McBride, THIS JOURNAL, **77**, 2751 (1955).

(7) G. F. Huttig, *Monatsh.*, **85**, 98, 365 (1954).

(8) J. Zawadzki and S. Bretsznajder, *Trans. Faraday Soc.*, **34**, 951 (1938).

amount of solid. For any constant pressure, the same conclusion follows from Fig. 3 since the half-time for a zero-order reaction is proportional to the initial amount of solid. For example, a comparison of the curves for a pressure of 282 mm. shows that the half-time increases from 1.6, 3.2, 6.8, 11.0, to 16.6 min. as the sample weight increases from 0.01, 0.02, 0.04, 0.08, to 0.16 g.

The data for thiourea may be treated in a strictly analogous manner except that the single family of curves shown in Fig. 3 is seen to be two families of curves in Fig. 4. This is evident if one considers the sample weighing 0.1527 g. and the curves corresponding to pressures of 246 and 283 mm.; these two curves intersect those corresponding to pressures of 188 and 213 mm. at relatively high ammoniation of the solid. This observation suggests that at higher pressures a competing process becomes rate-controlling when the extent of ammoniation is relatively great. It was also noted experimentally that at pressures much above 220 mm. a liquid phase was detectable in trace amounts.

In Fig. 7 the data for thiourea from Fig. 4 are treated in a manner analogous to that for urea. The discontinuity in Fig. 7 is accounted for on the basis of the formation of a supersaturated solution of the 1-ammoniate; this would correspond to the intersection of curve HH′ with curve FG at H″. The latter point represents a composition of 1 mole NH_3/mole NH_2CSNH_2 and a pressure of 220 mm. and corresponds to a supersaturated solution of the 1-ammoniate of thiourea. This pressure is in good agreement with the discontinuity in the kinetic data of Fig. 7, where the pressure p varies from 190 to 250 mm. Above and below this discontinuity the ammoniation is first order with respect to the ammonia pressure, $p - p_0$.[9] Since the discontinuity is not observed in the ammoniation of the smallest amount of thiourea used in any of these studies (0.0100 g.), the discontinuity must be related in some manner to the diffusion of ammonia through the solid. Finally it should be pointed out that the ammoniation of thiourea approaches zero order with respect to the initial amount of solid, S_0, with decrease in size of the sample ammoniated.

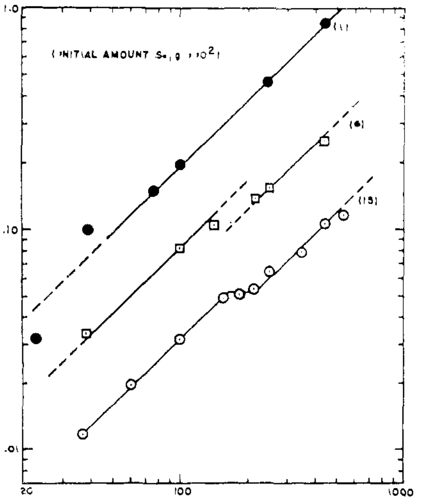

Fig. 7.—Differential rates of ammoniation of thiourea as a function of pressure.

The ammoniation of thiourea at 0.0° gave results generally comparable to those described above, and by considering systems having the same extent of surface reaction, 0.25 θ, the temperature coefficient of the ammoniation may be calculated. Winfield[10] and others have reported negative temperature coefficients for comparable cases, but according to Hinshelwood and Burk[11] the observed energy of activation is equal to the true energy of activation minus the heat of sorption of reactants plus the heat of sorption of retarding processes. Thus if the true heat of activation is small in relation to the heat of sorption of reactants (in the absence of any retarding process) the observed heat of activation would be negative. If equation 6 is used to calculate a constant for any given temperature, the heat of sorption of the reactants is automatically incorporated in the expression. However, if the equivalent expression obtained by substituting k_{-1}/p_0 for k_1

$$d(S{\cdot}NH_3)/dt = -d(S)/dt = k_{-1}(p - p_0)/p_0 \quad (7)$$

is used, the calculated energy of activation should be equal to the true energy of activation. For both urea and thiourea, this "true energy of activation" is equal to 0.5-1.0 kcal./mole.

The influence of the extent of surface reaction upon the rate of ammoniation remains to be considered. Since $n = 0$ in equation 1 for the Gibbs isotherm, the solid surface is assumed to be homogeneous and according to equation 4 the ammoniation should be zero order with respect to $1 - \theta$. Nevertheless, in Figs. 3 and 4 it is observed that the rate is not linear with time as would be expected if both θ and $1 - \theta$ have powers of zero, but that the rate decreases with increase in the extent of ammoniation. In Fig. 8 the differential rate for the ammoniation of urea plotted is as a function of the fraction of unammoniated solid, $1 - \theta$; this plot is essentially linear in the range 0.80 to 0.20 and over a more extended range as the pressure approaches

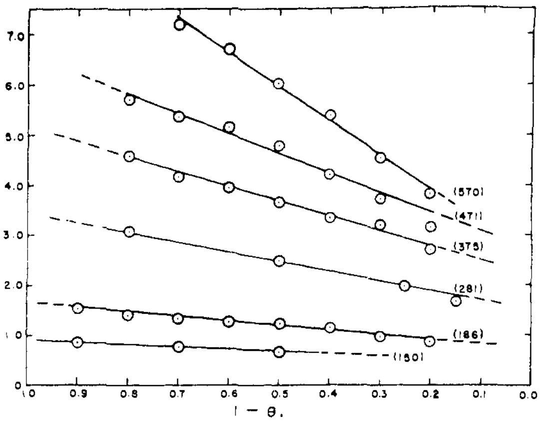

Fig. 8.—Differential rates of ammoniation as a function of the fraction of unreacted urea.

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[9] Similar studies (G. W. Watt and W. R. McBride, unpublished data) involving the ammoniation of ammonium chloride and ammonium sulfate to form the 3-ammoniates show that these reactions also are first order with respect to the ammonia pressure.

[10] M. F. Winfield, *Australian J. Chem.*, **6**, 221 (1953).

[11] C. N. Hinshelwood and R. E. Burk, *J. Chem. Soc.*, **127**, 1105 (1925).

the dissociation pressure. The reaction, however, is not zero order with respect to surface reacted, but more nearly 0.33 to 0.50. This might possibly represent a variation of equation 6 in which the function of $1 - \theta$ does not enter into the rate-controlling step. The decrease in rate is probably best attributed to a retardation process rather than explained on the basis of a fractional order for the Gibbs-type expression. From Fig. 8 for the two cases, $\theta = 0$ and $\theta = 1$, the ratios of the extrapolated values $(\theta = 0)/(\theta = 1)$, for the formation of the ammoniate of urea are 1.96, 2.23, 2.30, 1.96 or 2.36, and 2.40 corresponding to the pressures 150, 186, 281, 375 and 471 mm. As the pressure approaches the dissociation pressure it may be concluded that, within experimental error, the ratio approaches 2.00. In the equations[12] for processes retarded by a species A, the denominator of the expression for the differential rate is of the form $1 + K_2A$. If $K_2 = 1$, which is realistic in the present case, the effect of retardation may be incorporated into equation 7 as

$$d(S{\cdot}NH_3)/dt = -d(S)/dt = k_{-1}(p - p_0)/p_0(1 + \theta) \quad (8)$$

On the basis of this expression the differential rate should diminish to one-half of its original value as the fraction of surface ammoniated increases from $\theta = 0$ to $\theta = 1$. Thus, equation 8 is most likely the general form of the rate equation for reactions of this type in which *all of the solid present represents available surface.* This is apparently true in the case of the conditioned samples of urea and thiourea. By analogy, the rate equation for the initial ammoniation would be

$$d(S{\cdot}NH_3)/dt = -d(S)/dt = k_{-1}(p - p_0)(S)/p_0 \quad (9)$$

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[12] C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **127**, 327 (1925).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Thermomagnetic Analysis of Catalytically Active Nickel[1]

BY JEAN A. SABATKA AND P. W. SELWOOD

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The method of thermomagnetic analysis previously described has been improved by the construction of apparatus for *in situ* reduction and study of catalyst samples. It has been shown that massive and disperse nickel have the same magnetic moment at 0°K. The method has also been used for an investigation of several commercial nickel catalysts.

Introduction

In this article we describe apparatus developed for convenient measurement of specific magnetization over a wide range of temperature and for observing the effect of adsorbed gases on the magnetization. All chemical reactions on the catalyst samples are carried out *in situ*. There are also presented data relating to particle size distribution and to the influence of chemisorbed hydrogen for several different nickel catalyst preparations.

Experimental Part

Magnetic Balance.—A Faraday balance, similar to that previously described,[2] was adapted for use with ferromagnetic substances. The silica spiral spring was replaced with a beryllium bronze spring. The sample bucket and surrounding tubes were all made of silica to permit heat treatment and measurements to be carried out up to 1100°. The silica envelope was arranged so that hydrogen and other gases could be allowed to flow over the sample during heat treatment and during measurement. The upper end of the spring was supported through a metal bellows so that the sample could be moved in the magnetic field without access of air. The magnet was mounted on tracks so as to facilitate changing samples and replacement of a small furnace by appropriate shaped Dewar flasks. Higher temperatures were provided by a small sleeve furnace automatically controlled, while Dry Ice, liquid nitrogen and liquid hydrogen could be used for low temperatures. The fields used were about 6000 oersteds, which is more than adequate for saturation of massive nickel. The sample weight was such as to contain about 1 mg. of nickel. Pure massive nickel was used for calibration. All gases, such as hydrogen and helium, were purified before use. Helium was purified by passing it over supported reduced copper on asbestos at 600°, and then over silica gel at −190°. It was possible to maintain a high vacuum over the sample indefinitely, although less convenient to make actual magnetic measurements in vacuum.

Preparation of Samples.—The following commercial catalysts were studied: Girdler G-12 nickel catalyst, Harshaw Catalyst Ni-0107, Universal Oil Products Co. nickel hydrogenation catalyst, and Raney (W-6) nickel. Results also are given for a sample of nickel–silica co-precipitated catalyst prepared as described by Van Eijk Van Voorthuijsen and Franzen,[3] and designated by them CLA-5421, but here referred to as "Coprecipitate." Measurements were also made on a reduced mechanical mixture of coprecipitate and pure nickel oxide. This mixture, which was prepared before *in situ* reduction, contained equal weights of nickel from each of the two sources.

All samples except the Raney nickel were analyzed for nickel before reduction in the magnetic balance. The nickel weight per cent. found for the several samples was as follows: Girdler, 55.6; Harshaw, 67.9; U. O. P., 52.8; and coprecipitate, 42.2.

All samples except the Raney nickel were heated at 350° in flowing hydrogen for 24 hours. Some samples were further subjected to sintering as described below. After the samples were reduced the atmosphere was changed to purified helium and the specific magnetization was measured down to liquid nitrogen or liquid hydrogen temperatures as desired. The effect of chemisorbed hydrogen was determined by flushing the system with hydrogen at room temperature before the magnetization was measured.

A sample of coprecipitate was progressively sintered in flowing hydrogen up to 650° to determine whether the magnetization extrapolated to absolute zero is independent of particle size. This procedure is believed to be justified since the initial reduction is virtually certain to be complete[4] and it prevents reoxidation by traces of air or water vapor.

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[1] This is the second paper (other than a brief Communication) to be published on this topic. The first appeared in THIS JOURNAL, **77**, 1462 (1955). This work was supported under contract with the Office of Naval Research.

[2] P. E. Jacobson and P. W. Selwood, THIS JOURNAL, **76**, 2641 (1954).

[3] J. J. B. Van Eijk Van Voorthuijsen and P. Franzen, *Rev. trav. chim.*, **70**, 793 (1951).

[4] W. Heukelom, J. J. Broeder and L. L. Van Reijen, *J. chim. phys.* **51**, 473 (1954).