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120. Hisashi Nogami, Jun Hasegawa, Tsuneji Nagai, and Masatoshi Miyamoto: Studies on Powdered Preparations. IX.[1] Thermal Analysis of the Velocity of Reaction between Dried Aluminum Hydroxide Gel and Acid.[*2,3]

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It was described, in the previous papers,[1,2] that the reaction between dried aluminum hydroxide gel (DAHG) and acid was reproducible with satisfaction, although it had been considered that measurements on characteristic properties concerning powders were poorly reproducible. The purpose of the present study was to ascertain whether the same results would be obtainable by the different methods, henceforce an attempt to analyse the neutralization was made by the thermal measurement which exclude electrochemical factors observed at the measurement of pH.

Thermal analysis of reaction velocity is based on the calculation of reaction velocity from the measurement of continuous temperature change in the adiabatic reaction system.[3] The temperature change, dT, is represented by

$$dT=(Q/E)dx \qquad (1)$$

where E is the water equivalent of the system, Q the heat of reaction, and dx the change of the amount of a reactant. Assuming that the heat loss is in accordance to Newton's law, equation (1) is given as

$$dT/dt+\kappa\Delta T=(Q/E)(dx/dt) \qquad (2)$$

where ΔT is the temperature difference between the reaction system and the environment, κ the cooling constant, and dt the change of time. Since Q, E, κ, and ΔT are known and dT/dt is determined from the gradient of the plot dT *vs.* dt, the rate of reaction, dx/dt, can be calculated.

The equation to express the acid neutralizing velocity of DAHG given in the previous paper[2] is

$$-dH/dt=KWH^n \quad (0\leqq n<1) \qquad (3)$$

which shows that the rate of decrease of hydrogen ion concentration, $-dH/dt$, in the reaction between DAHG and acid is proportional to the quantity of DAHG, W, and the n'th power of hydrogen ion concentration, H. When an appropriately excessive equivalent of DAHG reacts with either hydrochloric acid or nitric acid, it is expected that the plot of temperature *vs.* time should be on a straight line because n approaches zero. In the case of sulfuric acid, however, the linearity of the plot will be lost, because n is about 0.5.

Experimental

Apparatus——1) A water bath with constant temperature: The temperature was controlled within a deviation of 0.001° at 28°, 38°, and 48° with Hg-acetone regulator.

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[*2] Taken in part from the thesis of Tsuneji Nagai for the degree of Doctor of Pharmaceutical Sciences, University of Tokyo, 1961.

[*3] Presented at the Kanto Local Meeting of Pharmaceutical Society of Japan, Tokyo, January 1961.

1) Part Ⅷ: This Bulletin, **10**, 741 (1962).

2) Part Ⅶ: H. Nogami, T. Nagai: *Ibid.*, **10**, 728 (1962).

3) S. Horiba, T. Ichikawa: Rev. Phys. Chem. Japan. **1**, 145 (1927).

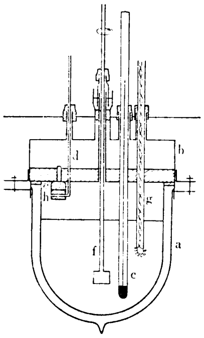

Fig. 1. Calorimeter

a : dewar vessel
b : lid
c : thermometer
d : glass rod
e : sample case
f : stirrer
g : heater
h : rubber stopper

2) Calorimeter : This is consisted of a Dewar vessel and a lid as shown in Fig. 1. A diameter of the Dewar vessel, *a*, is 11 cm. (inside) and 13 cm. (outside) with a depth of 10 cm. The lid, *b*, was a rubber disc covered with metal and equipped with a thermometer, *c*, a glass rod, *d*, connected to the sample case, *e*, a stirrer, *f*, and heater, *g*. *c* was a Beckmann thermometer graduated in 0.002° and vibrated for the smooth movement of mercury. *e* was a bell-shaped glass with a volume of 2 cc. The rubber stopper, *h*, was put off by pushing down *d* and the test sample of DAHG was suspended in the liquid. *f* was connected with a synchronized motor (500 r.p.m.) through a mercury pulley, and the distance between the top of the stirrer and the bottom of the vessel was always kept at 1.5 cm. The heater was composed of a platinum wire wound around a glass rod, and used for the determination of the water equivalent of the calorimeter and for heating the liquid in calorimeter to bring it to the equilibrium temperature.

Test Samples——Samples A and B which were the same as described in the previous papers[1,2] were used.

Procedure——1) Determination of the water equivalent and cooling constant : 300 cc. of distilled H_2O was pipetted into the calorimeter, warmed at 38°, and the system was left for 3 hr. in the thermostat with stirring to get a thermally equilibriated state. A definite electric current from alkaline cells was supplied to the heater, and the water equivalent was determined by measuring the rise of temperature. More than 3 hr. after cutting off the current, when the heat condition was considered to have become stationary, the descending temperature was measured as a function of time, and the cooling constant was determined.

2) Measurement of the reaction between DAHG and acid : 300 cc. of acid solution containing 0.5% Tween 80 was taken into the Dewar vessel, DAHG was put into the sample case, then lid and the Dewar vessel were closed tightly. In the same manner as described in 1), the calorimeter was allowed to stand for more than 3 hr. The sample case, *e*, was then opened to suspend test samples into acid solution, the rising temperature was measured, and the correction was examined according to equation (2).

Results and Discussion

The water equivalent and the Cooling constants were shown in Table I.

TABLE I. Water Equivalent and Cooling Constant of the System

Water equivalent (38°)	370.0 calories[a]
Cooling constant (28°)	3.85×10^{-3} deg./min.
(38°)	3.68×10^{-3} deg./min.
(48°)	3.76×10^{-3} deg./min.

a) The values at 28° and 48° are considered to be almost similar.

Preliminary examinations showed that the heat of wetting of DAHG and an influence of Tween 80 on the heat of reaction could be negligible.

As expected from the results of previous works,[1,2] the plot of temperature *vs.* time of the reaction between DAHG and hydrochloric acid gave the linear relationship which is shown in Fig. 2.

Therefore, it was found that the rate of emitting heat was independent from the concentration of hydrogen ion. The rapid heat emission at the initial stage of reaction

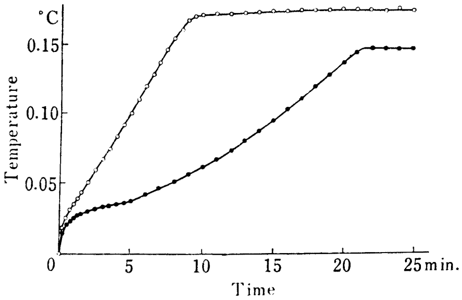

Fig. 2. Temperature Rise of the Reaction between DAHG and Hydrochloric Acid at 38° under 300 cc. of 0.020*N* Acid and 1.000 g. of Test Sample

-○- : sample A
-•- : sample B

seemed to be due to the heat of adsorption principally, and such a phenomena, had been observed by the measurement of pH change and discussed in the previous paper.[2] At the initial stage of the reaction, the curve of sample A become linear faster than that of sample B. The time, when the emission of heat ended, was called finished time,*[4] represented by t_∞ in this paper and obtained graphically from the plot of temperature *vs.* time. The values of t_∞ are shown in Tables II and III; the values of sample A were about a half of those of sample B. Therefore, it is understood that sample A was more reactive than sample B.

TABLE II. Finished Time, t_∞, of the Reaction between DAHG and Hydrochloric Acid, at 38° under 300 cc. of Acid

Concentration of acid (*N*)	t_∞ (Sample A) (min.)			t_∞ (Sample B) (min.)		
	(1.000)[a]	(0.800)[a]	(0.600)[a]	(1.000)[a]	(0.800)[a]	(0.600)[a]
0.025	11.8	14.4	19.5	24.9	30.2	40.0
0.020	9.7	11.3	15.2	21.4	25.8	32.2
0.015	7.3	9.2	11.6	17.8	20.9	26.0

a) (1.000), (0.800), and (0.600) show the quantities of test samples in g.

TABLE III. Finished Time, t_∞, of the Reaction between DAHG and Hydrochloric Acid, at 28° and 38° under 300 cc. of Acid and 1.000 g. of Test Sample

Concentration of acid (*N*)	t_∞ (Sample A) (min.)		t_∞ (Sample B) (min.)	
	28°	48°	28°	48°
0.025	33.3	5.1	75.8	9.6
0.020	29.3	4.0	66.5	8.1
0.015	23.7	3.3	56.2	6.5

Fig. 3 shows the influence of the kind of acid on the velocity of reaction. The plot of temperature *vs.* time of nitric acid was linear after the rapid temperature rise at the

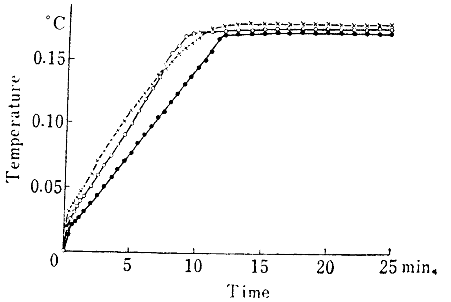

Fig. 3. Temperature Rise of the Reaction between DAHG and Hydrochloric Acid Nitric Acid and Sulfuric Acid at 38° under 300 cc. of 0.020*N* Acid and 1.000 g. of Sample A

-○- : hydrochloric acid
-•- : nitric acid
-×- : sulfuric acid

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*[4] In a strict sense of a word, the finished time, t_∞, is a slightly different from that described in previous papers.[1,2]

initial stage, but the gradient of the plot was a little less than that of hydrochloric acid. The curve of sulfuric acid was not linear and t_∞ was larger than that of the case of hydrochloric acid as listed in Table IV. These facts agreed well with the results in previous papers,[1,2] in which n in equation (3) was nearly zero in the cases of hydrochloric and nitric acids, and was about 0.5 in the case of sulfuric acid.

Table IV. Finished Time, t_∞, of the Reaction between DAHG and Sulfuric Acid or Nitric Acid, under 300 cc. of 0.020*N* Acid and 1.000 g. of Test Sample

Acid	Temperature	t_∞ (Sample A) (min.)	t_∞ (Sample B) (min.)
H_2SO_4	28°	30.0	71.0
	38°	11.5	25.7
	48°	5.1	10.5
HNO_3	38°	12.0	26.3

The velocity was not always additive with respect to the mixing ratio in the reaction between DAHG and mixed acids. The almost linear relationship in t_∞ with respect to the mixing ratio and no remarkable unevenness were observed in the mixture of hydrochloric acid and nitric acid as shown in Fig. 4, and the temperature-time curve corresponded to that of the case of original acid. On the contrary, in the mixture of hydrochloric or nitric acid and sulfuric acid, t_∞ became maximum at the ratio of about 5% of sulfuric acid (in gram-equivalent) as shown in Fig. 5; namely, at this ratio the reaction velocity became minimum. The shapes of the temperature-time curves were linear and similar to the case of hydrochloric acid (n was close to zero) when the concentration of sulfuric acid was lower than this ratio, and approached to sulfuric acid type (n was about 0.5) with an increase of the concentration of sulfuric acid in the mixture. It was considered that the order of the reaction changed remarkably at this ratio.

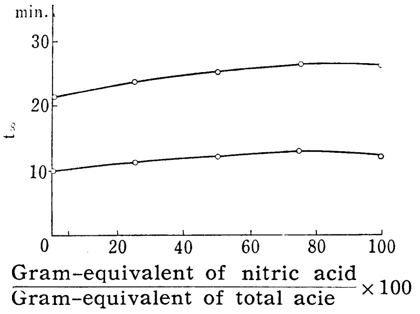

Fig. 4. Finished Time, t_∞, of the Reaction between DAHG and Hydrochloric Acid mixed with Nitric Acid at 38° under 300 cc. of 0.020*N* Acid and 1.000 g. of Test Sample

lower : sample A
upper : sample B

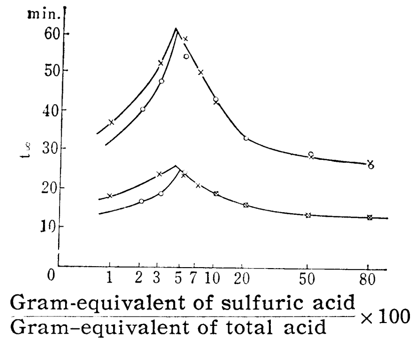

Fig. 5. Finished Time, t_∞, of the Reaction between DAHG and Hydrochloric Acid mixed with Sulfuric Acid and Nitric Acid mixed with Sulfuric Acid at 38° under 300 cc. of 0.020*N* Acid and 1.000 g. of Test Sample

lower : sample A
upper : sample B
-○- : hydorchloric acid+sulfuric acid
-×- : nitric acid+sulfuric acid

The reaction between DAHG and 0.020*N* hydrochloric acid containing the salt of 0.020 gram-equivalent per liter was examined. The curves of the reaction in the presence of chlorides, i. e., sodium chloride, magnesium chloride, or aluminum chloride, were hydrochloric acid type, and no effect of cations was observed. However, in the case of sulfates, i. e., sodium sulfate, magnesium sulfate, or alum, the curves lost such a linearity as found in the case of hydrochloric acid only, and the reaction velocities decreased, thus it corresponded to the case of sulfuric acid. These values of t_∞ were shown in Table V.

TABLE V. Finished Time, t_∞, of the Reaction between DAHG and Hydrochloric Acid mixed with Salt, at 38° under 300 cc. of 0.020*N* Acid containing Salt in the Concentration of 0.020*N* and 1.000 g. of Test Sample

Salt	t_∞ (Sample A) (min.)	t_∞ (Sample B) (min.)
NaCl	8.9	21.2
$MgCl_2$	9.0	20.0
$AlCl_3$	9.0	20.3
Na_2SO_4	12.2	25.0
$MgSO_4$	11.6	25.5
$KAl(SO_4)_2$	11.5	25.7

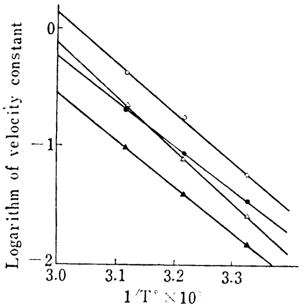

Fig. 6. Temperature Dependence of the Reaction between DAHG and Hydrochloric Acid and Sulfuric Acid

-○- : sample A and hydrochloric acid
-●- : sample A and sulfuric acid
-△- : sample B and hydrochloric acid
-▲- : sample B and sulfuric acid

TABLE VI. Activation Energy, E_A, of the Reaction between DAHG and Hydrochloric Acid or Sulfuric Acid

Acid	E_A (Sample A) (calories)	E_A (Sample B) (calories)
HCl	19,800	21,000
H_2SO_4	17,500	18,300

TABLE VII. Heat of Reaction, ΔH, between DAHG and Acid at 38°

Acid		ΔH (calories per gram-equivalent)	
		(Sample A)	(Sample B)
HCl		10,800	9,400
	(28°)	10,500	9,400
	(48°)	10,900	9,300
H_2SO_4		10,900	9,700
	(28°)	10,900	9,700
	(48°)	10,900	9,900
HNO_3		10,700	9,400
HCl with NaCl[a]		11,100	9,400
$MgCl_2$		11,000	9,600
$AlCl_3$		10,700	9,300
Na_2SO_4		10,700	9,400
$MgSO_4$		10,600	9,200
$KAl(SO_4)_2$		10,700	9,300

a) Salts added were equivalent to the acid concentration in normality unit.

Activation energy was estimated from Fig. 6 and shown in Table VI. The values were about 20,000 calories.

All the results mentioned above were in good agreement with those of previous papers.[1,2]

Heat of reaction was shown in Table VII. The values of sample A were always a little larger than those of sample B, and no effects with regard to the kind of acids and salts contained were observed. Those values corresponded to those in a critical table.[4]

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Summary

1. The reaction between dried aluminum hydroxide gel (DAHG) and acid was represented by

$$-dH/dt = KWH^n \qquad (0 \leqq n < 1)$$

where n is nearly zero is both cases of hydrochloric acid and nitric acid, and $0<n<1$ in the case of sulfuric acid by thermal analysis.

2. In the reaction between DAHG and hydrochloric acid mixed with sulfuric acid or nitric acid mixed with sulfuric acid, the order of the reaction, n, changed remarkably at the ratio of about 5% sulfuric acid (in gram-equivalent) and the reaction velocity was minimum at this ratio.

3. The activation energy of the reaction between DAHG and acid was found to be about 20,000 calories.

4. These facts mentioned above were in good agreement with the results of the pH measurement described in previous papers.

5. The heat of reaction, which agreed well with the values given in a critical table, was measured.

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[4] Nippon Kagaku-kai (Chemical Society of Japan): "Kagaku-Binran," p. 722 (1958), Maruzen, Tokyo.