ABSORPTION KINETICS OF HYDROGEN SULPHIDE USING ISOTHERMAL AND ISOVOLUMETRIC METHOD①

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ABSTRACT The experimental system for the study of the absorption kinetics of hydrogen sulphide under constant temperature and volume was set up. The macro-kinetic equation of the absorption process of hydrogen sulphide was determined and the overall rate constants of reaction at different absorption temperatures were evaluated. The apparent activation energy of absorption was calculated as 14.47 kJ·mol^{-1}. The hydrogen sulphide gas phase diffusion is deduced as the control stage of the absorption of hydrogen sulphide.

Key words hydrogen sulphide absorption kinetics isothermal and isovolumeric method

1 INTRODUCTION

In order to treat the industry waste gases, the process of absorption of low concentration hydrogen sulphide is used frequently. Therefore, investigation on the absorption kinetics of low concentration hydrogen sulphides is of pratical importance. Up to present, no report on the absorption kinetics of hydrogen sulphide by means of constant volume-pressure method has been found.

2 EXPERIMENTAL

2.1 *The Expression of Absorption Rate in the Isothermal and Isovolumeric Method*

The alkali absorption reaction of low concentration hydrogen sulphide at certain temperature is a process with the changeable gas mole number berfore/after reaction. The pressure of the system changes during the absorption process in an isothermal and isovolumetric reactor. With the measurement of the pressure of reaction system, the partial pressure of hydrogen sulphide can be obtained. Thus the rate of absorption process can be expressed as $r = -\mathrm{d}P_{t,\,H_2S}/\mathrm{d}t$.

2.2 *Apparatus*

The experimental set is shown in Fig. 1. The absorption reactor and absorption solution feeder was located in a thermostat. The "dead" volume of the reactor system should be as small as possible so that the volume of reactor system approximated the whole volume of the reaction system.

The absorption reaction of hydrogen sulphide with alkali solution was very quick. In order to investigate the absorption kinetics of this fast gas-liquid reaction, a measuring system, which could record the pressure of the reaction system automatically was consisted of a pressure gauge, a conductivity apparatus and a X-Y recorder etc.

Pressure gauge was a U-shaped device partially filled with dilute sodium chloride solution. One of its limbs, called measuring limb, had two parallel Pt-Re filaments used as electrodes to measure conductivity. The other limb, or level bottle, was 30 times larger in diameter than the measuring limb. So when the liquid level in measuring limb raised or dropped by tens of centime

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Fig. 1 Experimental system for the study of the absorption kinetics of hydrogen sulphide

1—reactor filled with hydrogen sulphide; 2—water-jacketed thermostat
3—alkali solution; 4—alkali solution injector; 5—pressure gauge;
6—Pt-Re filament electrode; 7—dilute sodium chloride solution;
8—level bottle; 9—X-Y recorder; 10—conductometer

tres, the liquid level in the level bottle was approximately constant and could be used as the "0" point of the liquid level in each measuring. Ignoring the effect of change of environmental temperature to the dilute sodium chloride solution's density and conductivity, the system pressure (p_s) was in proportion to liquid level difference between the two limbs, $p_s = p_0 - \rho g \Delta H$, and the solution's resistance between two electrodes was related to the liquid level in the measuring limb. The resistances of the sodium chloride solution at 298 K in the measureing limb were measured with a digital ohmmeter and the liquid levels were recorded. The results are shown in Fig. 2.

As shown in Fig. 2, the solution's resistance change ($R_t - R_0$) was in direct proportion to the liquid level change ($H_t - H_0$). So the pressure of reaction sytem could be measured by making the measurement of resistance. The resistance of solution was turned into voltage signal with a conductometer. The relationship between voltage signal(Y_t) and time(t) during the alkali absorption of hydrogen sulphide was recorded with an X-Y recorder. In fact, this relationship indicated the relationship between the system pressure ($P_{t,s}$) and time (t). From the

Fig. 2 The relationship between the liquid resistance change ($R - R_0$) and liquid level change ($H - H_0$) in the measuring limb

relationship of $Y_t \sim t$, the expression of the absorption rate was deduced as follows:

$$p_{t,\,H_2S} = p_{t,\,s} - p_{N_2} = p_0 - K(H_t - H_0) - p_{N_2}$$

$$\because (H_t - H_0) \propto (R_t - R_0) \propto (Y_\infty - Y_t)$$

$$\therefore p_{t,\,H_2S} \propto (Y_\infty - Y_t) \quad (1)$$

$$\because r = -\,dp_{t,\,H_2S}/dt$$

$$\therefore -\,dp_{t,\,H_2S}/dt \propto -\,d(Y_\infty - Y_t)/dt \propto -\,dY_t/dt \quad (2)$$

where $p_{t,\,H_2S}$ is the pressure of H_2S at time t, p_{N_2} is the pressure of N_2, p_0 is pressure of atmosphere, K is a constant.

2.3 *Reagents*

Sodium sulphide (AR) reacted with sulphuric acid solution to produce hydrogen sulphide gas was needed in the experiment. Alkali absorption solution was made up of sodium hydroxide (AR) and distilled water.

2.4 *Procedure of Experiment*

While the thermostat worked to keep the temperature of reaction system constant, nitrogen gas from a nitrogen cylinder was injected into the reactor to replace air. When the reactor became thermostatic, preparated hydrogen sulphide gas was injected into the reactor while the overall pressure of reaction system was kept at 100 kPa. After the reactor was filled fully with hydrogen sulphide gas, the reactor was closed. The conductometer and X-Y recorder determined the base point of the pressure of reaction system (namely the baseline of pressure measurment). After the baseline got stable, solution feeding valve was opened and sodium hydroxide solution was injected into the reactor using an injector. The solution feeding valve was closed immediately after injection.

During the process of the absorption of hydrogen sulphide under isothermal and isovolumic condition, the pressure measureing system recorded automatically the voltage signals (Y_t) via time (t). After the absorption process had finished, nitrogen gas was used to wash the reactor system.

3 DATA PROCESSING AND DISCUSSION

3.1 *Apparent Rate Constant of Absorption*

In each experiment, the mole number of alkali absorption solution was far greater than that of hydrogen sulphide gas. Therefore, the concentration change of alkali absorption solution at whole absorption process could be ignored. The surface chemical reaction of the absorption of hydrogen sulphide is quick[1]. The apparent rate equation of absorption could be expressed as

$$-\,dp_{t,\,H_2S}/dt = k(p_{t,\,H_2S})^n \quad (3)$$

where n is the reaction order, k is the apparent rate constant of absorption

From Eqn. (2) and (3) we have

$$dY_t/dt = k'(Y_\infty - Y_t)^n \quad (4)$$

The voltage signals (Y_t) at different time and the voltage signal (Y_∞) at the end of absorption were obtained from the voltage signal curve recorded automatically in experiments. For each experiment, ploting $\ln(Y_\infty - Y_t)$ against t gave a very good straight line. This showed a first order reaction proporty between the rate of alkali absorption reaction of hydrogen sulphide and the pressure of hydrogen sulphide, $n = 1$. The apparent rate constants of absorption at different temperatures could be calculated from the slope of the straight line(Table 1).

Table 1 Apparent rate constants at different temperatures

T / K	318	308	303	298	293
k' / $10^3\ s^{-1}$	1.61	1.36	1.24	1.14	0.99

3.2 *The Apparent Activation Energy of Absorption Reaction*

From the data in Table 1, ploting the natural logarithm of apparent rate constants of absorption($\ln k'$) against the reciprocal of temperature ($1/T$) gave a straight line(Fig. 3). The straight line equation was

$$\ln k' = 1.455 - 1773.27/T$$

According to Arrhenius' equation, we obtained the apparent activation energy of absorption reaction throught the slope of the straight line as:

E / kJ·mol^{-1} = 14.74

Fig. 3 $\ln k' \sim 1/T$ **relation curve**

3.3 *Control Stage of Absorption Process*

In 1964 Astrarita and Gioia[2] investigated the absorption kinetics of hydrogen sulphide in sodium hydroxide solution and in CO_3^{2-}-HCO_3^- ions buffer solution. Their investigation results showed that chemical absorption reaction of hydrogen sulphide was instantaneous reaction. Some other scientists[3-7] investigated the alkali absorption of CO_2 and SO_2, and all drew the conclusion that these gas-liquid reactions of acid-alkali neutralization were instantaneous reaction or quick reaction. So we can deduce that the surface chemical reaction procedure of alkali absorption of hydrogen sulphide is very quick, it has no prossibility to become the control stage of absorption process. A possible control stage is gas phase diffusion or liquid phase diffusion. Under the conditions of our experiments, the most posssible control stage of absorption process was gas phase diffusion because we took the concentration of hydrogen sulphide as that of industry waste gas and controlled it within low level (< 5%).

Experimental investigation on absorption kinetics of hydrogen sulphide under constant temperature and constant volume indicated that the rate of alkali absorption reaction of hydrogen sulphide against the pressure of hydrogen sulphide gas presented the first order reaction property. The absorption apparent activation energy was 14.47 kJ·mol^{-1}, which is within the range of the activation energy of gas diffusion. Thus we suggest that the hydrogen sulphide gas phase diffusion is the control stage of the absorption of hydrogen sulphide. Lin Yiying[8] also believes that hydrogen sulphide gas phase diffusion is the control procedure of absorption process.

REFERENCES

1 Onda K, Kobayashi T, Fujine M *et al*. Chem Eng Sci, 1971, 26: 2009.
2 Astrita G and *et al*. Chem Eng Sci, 1964, 19: 963.
3 Brainp L T, Beaverstock M C. Chem Eng Sci, 1965, 20(1): 47.
4 Hikita Haruo Asasatoru *et al*. Aich E Journal, 1977, 23(5): 538.
5 Danckwertsp V *et al*. Chem Eng Sci, 1963, 18(2): 63.
6 Blauwhoffp M M, Versteeg G F, Van Swaaijw P M. Chem Eng Sci, 1983, 38(9): 1411.
7 Astarita G *et al*. Chem Eng Sci, 1982, 37(5): 677.
8 Lin Yiying. Gas Absorption. Beijing: Metallurgy Industry Press, 1985: 15.

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