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A KINETIC STUDY OF CO₂ DESORPTION FROM THORIA*

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ABSTRACT

Desorption rate curves were obtained for carbon dioxide adsorbed on thorium at temperatures of 550°C, 450°C, 350°C, 250°C, 150°C, and 50°C. The gas was found to desorb according to a logarithmic law following initial rapid desorption. The logarithmic law may be shown to be operative if the activation energy for desorption varies linearly with surface coverage. A large apparent negative entropy of activation for desorption supports the fact that the adsorbed CO₂ is in a mobile state.

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** C. H. Pitt and M. E. Wadsworth are graduate student and Associate Professor, respectively, of the Department of Metallurgy, University of Utah. The results of this study will be submitted by C. H. Pitt in partial fulfillment of the requirements leading to the Ph.D. degree.

Introduction

The determination of the rate of desorption of gas from a solid surface has importance because of the information it can give about the state and nature of the surface. Desorption rate determinations have been widely used since work in this field first received impetus from investigations by Langmuir.¹ The following study deals with the determination of the desorption rate of carbon dioxide adsorbed on thoria. The variation of the activation energy of desorption with surface coverage is of special interest. This work was done following studies involving equilibrium adsorption work previously reported.² It is felt that fundamental information of this type is a valuable addition to the present data on the surface properties of thoria and will lead to a more complete understanding of the nature of the thoria surface and the mechanisms whereby it reacts with other substances.

Equipment and Procedure

The rates of desorption were determined by adsorbing carbon dioxide on the thoria at a pressure of 630 millimeters of Hg and subsequently applying a vacuum. Gravimetric measurement of the thoria at various time intervals was accomplished by measuring the extension of a quartz spring with a traveling cathetometer. The vacuum was attained using a mechanical roughing pump in connection with an oil diffusion pump. The specimen was placed in a platinum holder and heated to temperature in a Kanthal wound furnace which was automatically controlled by a Leeds and Northrup Model H-PAT controller. A diagrammatic sketch of the important components of the equipment used in this study is shown in Figure 1. Two three-inch quartz springs were used in series having a combined spring constant of 0.00649 inches per milligram. The sample was suspended from the quartz springs by quartz fibers

which were drawn to about 0.03 centimeters in diameter. The platinum holder consisted of four tiers of platinum foil, circular in shape and 3/8 inches in diameter. About one gram of thoria was carried by the holder. A zircum tube was used as the containing tube in the sample area. The temperature measuring device was a Model 8667 Leeds and Northrup potentiometer using a chromel-alumel thermocouple with an ice bath cold junction. The thermocouple was introduced into the system by tungsten leads fused through the glass.

Approximately one gram of thoria was measured into the platinum sample holder and weighed to the nearest milligram. The sample was then placed in position and evacuated to less than 10 microns pressure. With the vacuum connected to the system the sample was heated to the outgassing temperature (650°C). By the time temperature equilibrium was attained the pressure was less than 10 microns. A pressure of 600 mm CO₂ was then admitted to the sample chamber and held for approximately one minute. The chamber was then evacuated and held at the degassing temperature and three microns pressure for one hour. The temperature was then lowered to the desired desorption temperature, the vacuum being maintained during the lowering. After the temperature was reached the roughing pump was removed from the system, and 630 mm pressure of CO₂ was admitted to the system. At this point the vacuum pumps were kept in operation but not connected to the system. After gas adsorption had ceased the vacuum pumps were again connected to the system and desorption initiated. Zero time was taken at the instant that 500 microns pressure was attained in the system. It took approximately 90 seconds to reach this pressure. Cathetometer readings were taken at suitable intervals. Due to the vacuum and initial conditions, considerable "bobbing" of the sample occurred, and precise readings were difficult to obtain at the beginning of the run. The "bobbing" was partially overcome by attaching a small

length of alumel wire to the quartz fiber and using a permanent magnet outside of the system as a brake. If too much movement was present at the start of the run it was repeated until better conditions prevailed.

Results

Desorption rate data were obtained at temperatures of 550°C, 450°C, 350°C, 250°C, 150°C, and 50°C for a degassing temperature of 650°C. The data obtained are shown in Table I in the appendix. These results are plotted in Figures 2 and 3 showing the linear relationship of the change in surface coverage (θ) with the logarithm of time. The fraction of surface covered (θ) was calculated by assuming that 16 mg. of CO_2 would be adsorbed on the particular site in question for full surface coverage. This is in accord with surface area and equilibrium adsorption determinations. The initial portions of the curve were difficult to determine accurately due to the sudden withdrawal of gas from the system and the sensitive movement of the quartz spring assemble. The curves may be divided into three parts. In the first part the gas was removed rapidly and measurement was difficult. In the second portion the amount of gas desorbed was directly proportional to the log of time. In the third part the amount of gas desorbed decreased rapidly, and practically no more gas could be removed even with long pumping times. In some cases pumping was continued for 36 hours with no measurable amount of gas removed after the first two hours.

Theory

In 1929 Becker³ found that the equation $-\frac{d\theta}{dt} = c\theta e^{b\theta}$ described the rates of desorption of cesium atoms and ions from a tungsten surface. Here b and c are constants and θ is the fraction of surface covered. An exponential function such as this is required to fit observed desorption data.

Taylor⁴ first pointed out clearly that if the activation energy is E and the heat of adsorption is Q , the rate of desorption is proportional to $e^{-\frac{(E+Q)}{RT}}$. Subsequent to this time practically all desorption rates dealing with chemisorbed gases have been shown to follow an exponential form. In this respect the application of the theory of absolute reaction rates⁵ to desorption studies has proven valuable. It is not expedient that each study of similar nature be reviewed although several such studies have been carried out.^{6,7,8,9}

According to absolute reaction rate theory we may write for the rate of desorption:

$$\frac{d\theta}{dt} = -k_0' \theta \frac{kT}{h} e^{-\frac{\Delta F^\ddagger}{RT}} \quad (1)$$

where θ = fraction of surface covered, $\Delta F^\ddagger$ = activation energy for desorption, T = absolute temperature, k_0' = constant which is directly related to the number of sites per square centimeter of sample area, k , h , R = Boltzmann, Planck, and gas constants. In equation (1) kT/h has the dimensions of frequency, k_0' is a concentration term, and $e^{-\Delta F^\ddagger/RT}$ is a probability factor dealing with the formation of the activated complex. The term $\Delta F^\ddagger$ need not be a constant but may vary linearly in certain cases with surface coverage.

The linear variation of $\Delta F^\ddagger$ with surface coverage has been explained in two ways. Cook, Pack, and Oblad¹⁰ have proposed that the unattached valence bonds at the surface of a solid are in a high energy state which can be relieved or minimized by adsorption. This strain is distributed throughout the surface and would involve a linear variation of free energy of activation with increasing energy as desorption proceeds. Higuchi, Ree, and Eyring⁸ have proposed a model which involves the formation of a surface double layer and subsequent surface repulsion of adsorbed ions which also

leads to a linear variation of activation energy with surface coverage. The linear variation of $\Delta F^\ddagger$ with surface coverage is common in solid gas systems and provides a fairly accurate evaluation of the data obtained in the present study.

The linear variation may be expressed by the equation:

$$\Delta F^\ddagger = \Delta F_0^\ddagger - \alpha \theta \quad (2)$$

By proper manipulation of equations (1) and (2) (see appendix for derivations) one can arrive at the result:

$$\Delta \theta = \frac{2.3 \cdot RT}{\alpha} \log t + K \quad (3)$$

where K is a constant for a particular temperature and $\Delta \theta$ is the fraction of surface from which gas has been removed during desorption. The assumptions made in obtaining equation (3) do not hold for the extreme values of θ , and consequently the equation breaks down for very short and very long times of desorption. However, for middle values of θ the data follow a linear relationship for a plot of $\Delta \theta$ versus $\log t$ as can be seen from Figure 2. The fact that the lower temperature (50°C and 150°C) show increasing amounts of gas desorbed may be explained by realizing that there are two different sites operative, one of which is effective only at low temperatures.² Hereafter the site which becomes effective at low temperatures will be designated as site 2 as compared with site 1 which will adsorb gas at all temperatures. If the amount adsorbed on site 2 is calculated and subtracted from the experimentally determined desorption rates at 50 and 150°C, these low temperature desorption curves fall below the high temperature curves as shown in Figure 4. The amount initially adsorbed on site 2 adsorption centers can be calculated from the equation:

$$\log \frac{(1-\theta)}{\theta} - \frac{\alpha\theta}{2.3 RT} = \frac{\Delta F_o}{2.3 RT} - \log P_{CO_2} \quad (4)$$

where ΔF_o and α are known from equilibrium adsorption measurements.² From the curves in Figure 4 and equation (3), values for α from the desorption rate curves can be calculated. These α_1 values are effectively those for desorption from site 1 adsorption centers. A graphical comparison of the α_1 values obtained from equilibrium adsorption measurements and desorption rate curves is shown in Figure 5. The close correspondence between these values indicates that the amount of surface coverage has little effect on the energy state of the activated complex, and that the linear variation of ΔF with surface coverage results mainly from the variation of the enthalpy of adsorption with surface coverage.

Based upon this model it is possible to calculate the enthalpy and entropy of activation involved in the desorption process. The enthalpy of activation may be obtained by means of equation (3) (as shown in the appendix). The final equation obtained which is derived for a specific time of 100 seconds is:

$$\left[\frac{\alpha\theta}{T} + 2.3 R \log \alpha\theta \right]_{t=100} = \frac{\Delta H_o^\ddagger}{T} - K' \quad (5)$$

where K' is a constant which includes the entropy of activation and $\Delta H_o^\ddagger$ is the enthalpy of activation. A plot of this equation is shown in Figure 6 from which a value of 22,500 calories was obtained for $\Delta H_o^\ddagger$. The entropy of activation may now be obtained in two ways. First it may be evaluated by substituting for K' in equation (5)

$$K' = 4.6R + \Delta S_o^\ddagger + 2.3R \log \frac{k_o^\ddagger k}{Rh} \quad (6)$$

and solving for $\Delta S_o^\ddagger$, all other quantities in the equation being known constants. The constant $k_o^\ddagger$ is the number of sites per square centimeter.

This constant must be corrected for the units in which the rate has been expressed. The rate being expressed in $\Delta\theta/\text{gm-sec}$, the corrected value for k_o' is then

$$k_o' = 1.37 \times 10^{-15} k_o \quad (7)$$

The value used for k_o was 1×10^{15} sites/cm². Substituting these values in equation (5), $\Delta S_o^\ddagger$ was found to be -53 e.u. Secondly a value for $\Delta S_o^\ddagger$ may be determined directly from equation (1) by measuring the actual rate graphically and using the equation:

$$\Delta F^\ddagger = \Delta H_o^\ddagger - T\Delta S_o^\ddagger - \alpha\theta \quad (8)$$

The value obtained for $\Delta S_o^\ddagger$ in this manner was -51.5 e.u. One would expect the entropy of desorption at first sight to be a low value near zero. On the other hand a large negative entropy may be expected if the adsorbate is in a highly mobile state on the surface. This being the case it is entirely possible that in order for desorption of CO₂ to occur the mobile carbonate ion must assume a special configuration which consequently involves a high negative entropy. It may be instructive to calculate some of the energy relationships involved for a particular temperature and surface coverage. A representation of the energy relationships for various values of θ at a temperature of 350°C is shown in Figure 7. In this case the activation energy for desorption at zero surface coverage was 55 Kcal and the free energy of desorption -12.4 Kcal. As the surface fills up, the diagram indicates the changes which take place in the desorption activation energy and the free energy of adsorption. In Figure 6, θ , the fraction of surface covered, would not become much larger than about 0.32 since at this point the free energy of adsorption becomes positive. It may appear from the energy relationships that the rate of adsorption would be near that of desorption. This is only true at high surface coverages.

Summary and Conclusions

The desorption of carbon dioxide from thoria was found to occur rapidly at first and then follow a straight line function expressed by a plot of $\Delta\theta$ (change in surface coverage) versus the log of time. After 30 minutes to an hour desorption virtually ceased for the temperature range studied. Application of the theory of absolute reaction rates to the data indicates that the activation energy for desorption varies linearly with surface coverage, providing a basis for the linear relationship found. The enthalpy and entropy of activation were calculated and found to be respectively 22,500 calories and -53 e.u. The high negative entropy is unusual but may be possible because of the presence of CO_2 on the surface in a mobile state. Desorption rate studies correlate closely with results obtained for the equilibrium adsorption of CO_2 on thoria in that in each case there is a linear variation of free energy with surface coverage. Two types of surface sites appear to be involved with the CO_2 in a highly mobile state on the surface.

APPENDIX A

Derivation of Desorption Rate Equations

The rate of desorption may be expressed by the equation

$$\frac{d\theta}{dt} = k_o \frac{kT}{h} \theta e^{-\Delta F_o^*/RT} e^{\alpha\theta/RT} \quad (1)$$

This may be written

$$\frac{d\theta}{dt} = A e^{\alpha\theta/RT} \quad (2)$$

Where $A = k_o \frac{kT}{h} \theta$ and θ is considered essentially constant in this expression. Integrating equation (2) results in the expression

$$\frac{-RT}{\alpha} e^{-\alpha\theta/RT} = -At + C \quad (3)$$

Using the boundary condition $t = 0$ at $\theta = \theta_o$ gives

$$C = \frac{-RT}{\alpha} e^{-\alpha\theta_o/RT} \quad (4)$$

Substituting (4) into (3) and rearranging,

$$e^{\alpha(\theta_o - \theta)/RT} = \frac{\alpha At}{RT} e^{\alpha\theta_o/RT} + 1 \quad (5)$$

Assuming $\frac{\alpha At}{RT} e^{\alpha\theta_o/RT} \gg 1$ as t increases and taking the log of both sides of equation (5) results in the equation,

$$\frac{\alpha\Delta\theta}{RT} = \ln t + \ln \frac{\alpha A}{RT} e^{\alpha\theta_o/RT} \quad (6)$$

or

$$\Delta\theta = \frac{RT}{\alpha} \ln t + \frac{RT}{\alpha} \ln \frac{\alpha A}{RT} e^{\alpha\theta_o/RT} \quad (7)$$

which may be written in condensed form as

$$\Delta\theta = \frac{2.3 RT}{\alpha} \log t + K \quad (8)$$

where K is constant at a given temperature and is equal to the last term of equation (7). Using equation (7) for $t = 100$ sec results in the expression

$$\Delta\theta_t = 100 = \frac{RT}{\alpha} 2 \times 2.3 + \frac{RT}{\alpha} \ln \left(\frac{\alpha A}{RT} e^{\alpha\theta_0/RT} \right) \quad (9)$$

Substituting the value for A in equation (9) and using the relationship

$$\Delta F_o^\ddagger = \Delta H_o^\ddagger - T \Delta S_o^\ddagger \quad (10)$$

gives the equation

$$\frac{\alpha\theta}{T} + R \ln \alpha\theta = \frac{\Delta H_o^\ddagger}{T} - K' \quad (11)$$

where

$$K' = 4.6R + \Delta S_o^\ddagger + R \ln k_o k/Rh \quad (12)$$

In equation (2), θ is considered a constant which is an approximation justified only by the fact that θ appears in the exponent and that we do not deal with very large or very small values of θ . Equations such as equation (1) can be solved also by the use of prepared tables¹¹, but this method is tedious and does not add appreciably to the final results.

APPENDIX B

Table I: Desorption Rate Data for CO₂ Adsorbed on Thoria

T = 550°C		T = 450°C		T = 350°C		T = 250°C		T = 150°C		T = 50°C	
$\Delta\theta^*$	t	$\Delta\theta$	t	$\Delta\theta$	t	$\Delta\theta$	t	$\Delta\theta$	t	$\Delta\theta$	t
.136	30	.065	30	.057	30	.034	30	.095	30	.186	30
.136	45	.091	45	.077	45	.063	45	.117	45	.210	60
.141	75	.096	60	.094	60	.091	60	.123	60	.219	90
.157	105	.106	75	.101	75	.103	120	.134	90	.239	120
.168	135	.117	90	.108	90	.106	150	.146	120	.243	150
.177	165	.123	105	.114	105	.116	210	.153	150	.250	180
.184	210	.132	120	.118	120	.121	270	.159	180	.261	240
.192	270	.136	135	.125	135	.129	390	.164	240	.273	300
.209	330	.141	150	.128	150	.138	510	.173	300	.277	360
.216	390	.146	180	.134	180	.145	630	.179	360	.287	480
.223	510	.151	210	.139	210	.151	810	.187	480	.292	600
.228	630	.161	270	.143	255	.153	1110	.191	600	.296	720
.235	810	.170	330	.156	375	.156	1410	.198	900	.302	900
.239	1110	.180	390	.170	630	.163	1710	.199	1200	.307	1200
.241	1410	.183	450	.181	810	.170	2310			.307	1500
.247	1710	.190	510	.188	1110	.171	2910			.310	1800
.254	2010	.198	630	.197	1410						
.259	2310	.209	810	.205	1710						
.259	2610	.218	1110	.207	2110						
.259	2910	.225	1410	.216	2400						
		.233	2010	.217	2700						
		.233	2310								
		.233	2610								
$\theta_0 \rightarrow$	.308		.348		.362		.381		.405		.577

* θ calculated on the basis that 16 mg. of CO₂ will completely cover site-one sites.

APPENDIX C

Table II: Calculated α_1 Values Determined from Rates of
Desorption of CO_2 on Thoria

Temperature °C	$\frac{1}{T}$	$\theta(\text{site 1})$ for $t=100$	α_1 Equilibrium ² Adsorption	α_1 Desorption	$\frac{\alpha\theta}{T} + 4.6 \log \alpha\theta$
550	1.215	0.155	37,000	38,200	24.55
450	1.383	0.226	37,100	35,000	28.95
350	1.605	0.251	37,500	37,700	33.50
250	1.912	0.285	37,600	38,800	39.0
150	2.364	0.337	37,800	39,000	50.1
50	3.095	0.397	38,000	39,000	67.1

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Figure 1. Diagrammatic sketch of experimental equipment.

Figure 2. Desorption rate versus log time for CO_2 desorption from thoria.

Figure 3. Desorption rate versus log time for CO_2 desorption from thoria.

Figure 4. Desorption rate plots of CO₂ from thoria considering site one sites only.

Figure 5. Comparison of α values for site one sites obtained from desorption rate and equilibrium adsorption measurements of CO₂ on thoria.

Figure 6. Plot of equation 5 from which the enthalpy of desorption of CO_2 from thorfa is obtained.

Figure 7. Diagram of free energy relationships between free energy of adsorption, free energy of activation for desorption and surface coverage for CO_2 on thorfa at 350°C .

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