JOURNAL OF CATALYSIS **1**, 208–215 (1962)

On the Energetic Heterogeneity of Clean Evaporated Nickel Films Studied by Means of the Place Change Between Adsorbed Isotopic CO Molecules

R. SUHRMANN, HJ. HEYNE, AND G. WEDLER

From the Institut für Physikalische Chemie und Elektrochemie der Technischen Hochschule, Hannover, Germany

Received December 29, 1961

The adsorption of $C^{12}O^{16}$, $C^{13}O^{16}$, and $C^{12}O^{18}$ was used to study the energetic surface heterogeneity of evaporated Ni films. The isotopic gases were adsorbed one after the other and the gas phase was analyzed mass spectrometrically. If the gases were adsorbed at 77°K, the equilibrium between gas phase and adsorption phase was obtained between 90° and 195°K. The temperature at which the equilibrium is reached is lowest for the molecules adsorbed at high coverages and highest for the molecules adsorbed on the clean film indicating differences in adsorption energies of the film surface concerning the adsorption of CO.

If the successive adsorption of the three isotopic gases took place at 273°K, no difference in the behavior of the isotopic gases could be observed, indicating that the mobility of the adsorbed molecules is large enough to overshadow the influence of surface heterogeneity.

An isotopic exchange between the atoms of the adsorbed molecules could not be observed.

INTRODUCTION

When carbon monoxide is adsorbed by an evaporated Ni film the film resistance at first increases rapidly with coverage, and gradually reaches a limiting value before the monolayer is complete (*1*). Similarly the heat of adsorption is large and constant (32 kcal/mole) at low coverages and then falls to small values at higher coverages (*2*). This behavior may be explained in two ways:

(1) If the surface were homogeneous the adsorption of molecules would be statistically distributed. There would be no mutual interaction between the adsorbed molecules at low coverages, whereas there would be an increasing interaction with increasing coverage leading to a decrease in the specific effects between the molecules and the adsorbing surface (induced heterogeneity).

(2) The behavior mentioned above also could be explained by a heterogeneity of the unoccupied surface on which there would be centers leading to a strong binding of the adsorbed molecules and other centers leading to weak bonds. As in case 1 an induced heterogeneity will be superposed at high coverages.

In order to decide whether the unoccupied surface of evaporated Ni films is homogeneous or heterogeneous and to investigate the influence of the mobility of the adsorbed molecules, we have studied the adsorption of CO using the isotopic gases $C^{12}O^{16}$, $C^{13}O^{16}$, $C^{12}O^{18}$. It is to be expected that these gases will show no isotopic effects in relation to the surface bond.

Similar considerations were made by S. S. Roginski and co-workers (*3*). Experiments have been performed with powdery Fe catalysts (*4, 5*) using radioactive $C^{14}O$, with powdery Ni catalysts (*6, 7*) and evaporated Ni or W films (*7*) using H_2 and D_2, and with Pt films using H_2, D_2, and T_2 (*8*). Recent experiments with H_2 and D_2 have been performed by Gentsch on extremely pure Pt (*9*) and Ni films (*10*); in this work the gas phase was analyzed by means of an omegatron.

EXPERIMENTAL METHOD

Preparation of the Isotopic Gases

In the preparation of $C^{12}O^{16}$, $Ca(C^{12}O_2)_2$ was thermally decomposed in bulb D (Fig. 3).

To prepare $C^{13}O^{16}$, $BaC^{13}O_3$, enriched in C^{13} to 57.1% was employed. $C^{13}O_2$ was developed by addition of $HClO_4$ in the evacuated apparatus shown in Fig. 1. The water vapor was condensed in traps connected to A and cooled by solid carbon dioxide. The developed carbon dioxide was condensed in an ampule cooled by liquid nitrogen. Gases not condensable at this temperature were pumped off. The ampule with carbon dioxide was sealed off and connected to an evacuated tube filled with Zn grains in order to reduce the carbon dioxide to carbon monoxide at 400°C. The reduction was controlled by means of mass spectrometric analysis which indicated that after the condensation of residual carbon dioxide, the content of the carbon monoxide was 56.3% $C^{13}O^{16}$ with a contamination by H_2 smaller than 0.1%. The carbon monoxide was sealed off in ampules with glass skins which could be magnetically smashed.

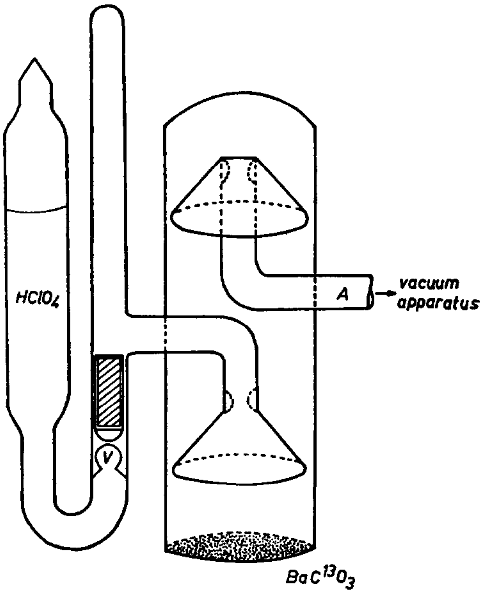

FIG. 1. Cell for preparation of $C^{13}O_2$.

The basic substances in the preparation of $C^{12}O^{18}$ were H_2O^{18} (90 atomic % O^{18}) and graphite. The oxygen was developed by electrolysis of H_2O^{18} in the cell shown in Fig. 2. The cell was joined at R_K to the vacuum apparatus. The bulbs K_A and K_K contained NaN_3 which was thermally decomposed to produce a Na film in N_A and N_K. Nitrogen was pumped off and K_A and K_K were sealed off. From an ampule connected to R_K H_2O^{18} was sublimed and collected on the glass tips cooled by liquid nitrogen in D_A and D_K. During the above process the water vapor in the system reacted with the Na film. The hydrogen produced by this reaction was pumped off and the anode and cathode compartments were separated at S. After warming of D_A and D_K the water on the tips under D_A and D_K dripped into the anode and cathode compartments, A and K, separated by a clay pin, D, sealed in a glass skin, W. At E_A and E_K the Pt electrodes were connected with tungsten wires sealed in glass. After the electrolysis, oxygen was sealed off in ampules connected to R_A. The oxygen was contaminated with 0.1% H_2. The concentration of O^{18} was 89.8 atomic %.

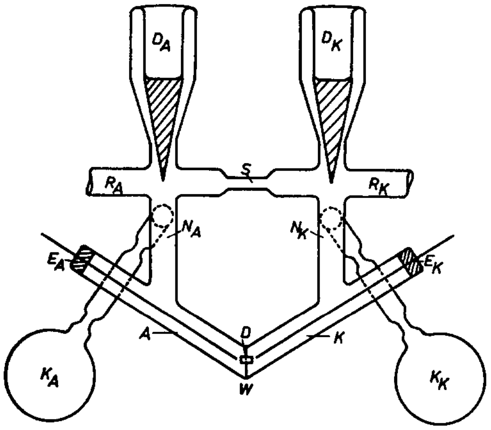

FIG. 2. Apparatus for electrolysis of H_2O^{18}.

$C^{12}O^{18}$ was prepared by reaction of O_2^{18} with a glowing graphite pin at 800°C. Carbon dioxide was condensed at 77°K. $C^{12}O^{18}$ was sealed off in ampules. The composition of the carbon monoxide was

$C^{12}O^{16}$	10.2%
$C^{13}O^{16} + C^{12}O^{17}$	1.3%
$C^{12}O^{18}$	87.5%
$C^{13}O^{18}$	1.1%
H_2	<0.1%

Apparatus

A scheme of the vacuum apparatus used in this investigation is shown in Fig. 3.

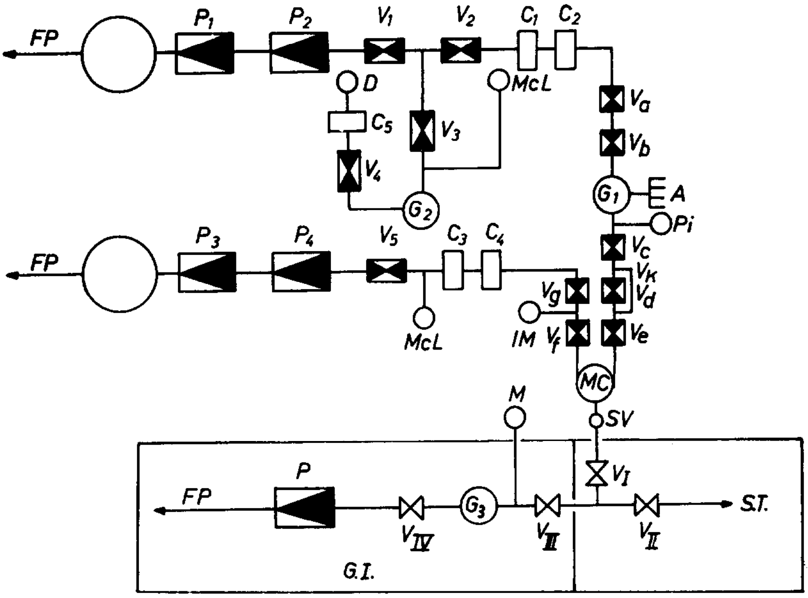

FIG. 3. High vacuum apparatus.

The cell (MC) for the evaporation of the Ni film is connected with the mercury diffusion pumps, P_3 and P_4, by the two greaseless ball joint valves, V_f and V_g. The pressure can be measured by the McLeod gauge, McL, or the ionization gauge, IM. The ball joint valve, V_e, connects MC with the dosing system between V_e and V_a.

The ampules, A, containing the isotopic gases can be opened magnetically. The pressure in the volume G_1 is monitored by the Pirani gauge, P_i. In order to admit the gas, the ball joint valves V_c and V_e are opened so that the gas passes either through the capillary tube V_k when V_d is closed or directly through when V_d is opened.

The gas can also be developed in bulb *D* and reaches G_2 through the mercury cutoff, V_4. Its pressure is measured by the McLeod gauge, McL. The gas can be conducted through the mercury cutoffs, V_3 and V_2, and the cooling traps, C_1 and C_2, into the dosing system.

SV is a valve which can be opened by magnetically smashing a glass skin. It connects the measuring cell with the mass spectrometer (Atlas CH3). M is a membrane microgauge in the gas inlet system, G.I., of the spectrometer. S.T. is the separation tube.

The whole apparatus can be outgassed at 300°C.

The measuring cell, MC, is shown in Fig. 4. It consists of a bulb intersected by four tubes. The left tube contains the electrical lead in wires for the evaporating Ni coil. The electric resistance of the evaporated film is measured by means of two Pt contact foils, Pt melted on the glass. The lead-in wires for the foils pass through two tubes, R, positioned in front and in back of the large center tube. The gas is

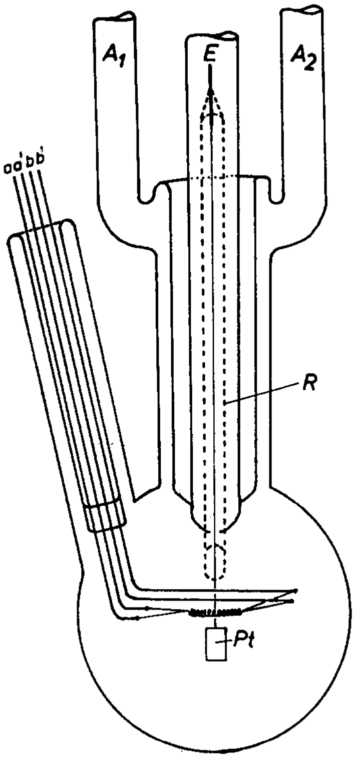

FIG. 4. Measuring cell.

added through the tube E; A_1 and A_2 lead to the mass spectrometer and to the pumping system. The area of the evaporated film was 500 cm². Since CO is also adsorbed by the glass surface it is important that the ratio of film surface area to glass surface area is as large as possible. The amount of CO adsorbed on the glass surface was determined in a blank test.

The Ni was evaporated at 77°K at a pressure lower than 10^{-9} mm Hg until the resistance of the resulting film was 100 Ω and annealed for one hour at 100°C.

RESULTS

Adsorption at 77°K

The annealed Ni film was cooled to 77°K and an initial known quantity of $C^{12}O^{18}$ was introduced into the cell* through the capillary tube, V_k. The amount adsorbed at a given time could be calculated from the decrease in pressure in G_1 (Fig. 3). At the same time the resistance of the film was measured. Figure 5 shows the increase in resistance as a function of coverage. At point A all $C^{12}O^{18}$ was adsorbed. The equilibrium pressure, p, was 1×10^{-8} mm Hg. Then in the same manner a known quantity of $C^{13}O^{16}$ was admitted (A to B, Fig. 5; $p = 5 \times 10^{-8}$). From B to higher coverages several known quantities of $C^{12}O^{16}$ were added from G_2 (Fig. 3) until p was 4.9×10^{-3} mm Hg. After point B in Fig. 5 the resistance reached a maximum and then decreased to smaller values. The smooth shape of the resistance curve shows that no isotopic effect was observed.

The composition of the gas phase is shown in Table 1; t_a indicates a measurement made immediately after either a gas introduction or a temperature change, and $t_{(x)}$ indicates a measurement made after a time lapse of (x) minutes. Column U indicates the number of all molecules (adsorbed *and* in the gas phase) and column V the number of the molecules in the gas phase alone.

If the thermodynamic equilibria in the adsorption phase and between adsorption phase and gas phase had been attained, the figures in column V/U would have been equal for $C^{12}O^{18}$, $C^{13}O^{16}$, and $C^{12}O^{16}$. However, that is not the case at 77°K. Also when the temperature of the film is raised to 90°K the equilibrium is not reached. Only when the temperature is 195° or 273°K are the figures in column V/U equal, showing that the system equilibrates.

The small values of V/U for $C^{12}O^{18}$ and $C^{13}O^{16}$ compared with $C^{12}O^{16}$ seem to indicate that $C^{12}O^{18}$ and $C^{13}O^{16}$ are more strongly bound to the surface than $C^{12}O^{16}$. But this statement is not valid because of the uncertainty that all $C^{12}O^{16}$ molecules take part in the equilibrium. It might be possible that the heat of desorption cannot be supplied at such a low temperature even

---

* Hereafter symbols $C^{12}O^{18}$, $C^{13}O^{16}$, and $C^{12}O^{16}$ do not denote the pure isotopic gases but the mixture enriched in the three isotopic components with a composition as described in the section on Experimental Methods.

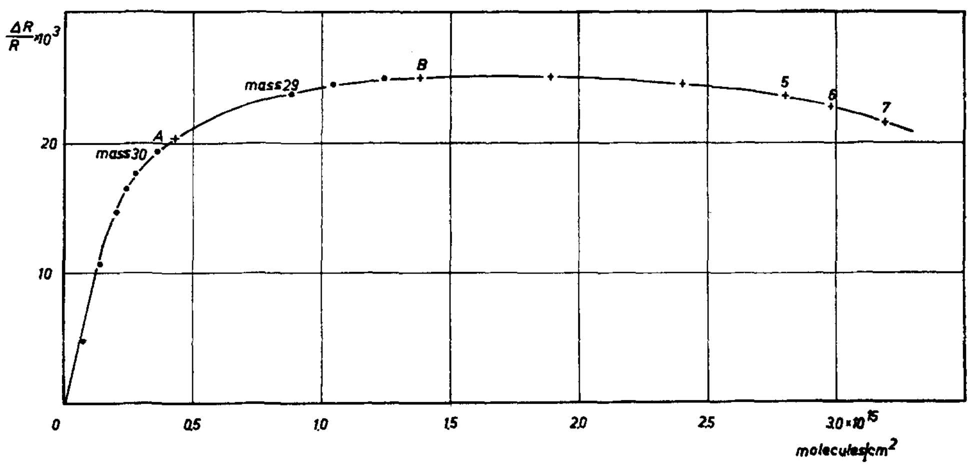

FIG. 5. Relative change in resistance as a function of coverage at $T = 77°K$. $C^{12}O^{18}$ was adsorbed until point A was reached and $C^{13}O^{16}$ until B was reached. $C^{12}O^{16}$ was adsorbed thereafter. The additions 5, 6, and 7 refer to the three lines in Table 1.

for the most weakly bound molecules. The fact, however, that the values of V/U for $C^{12}O^{18}$ are smaller than those for $C^{13}O^{16}$ indicates that the strength of the bond between molecule and surface depends on the state of precoverage of the surface.

The latter result is confirmed by an experiment shown in Fig. 6. In this experiment the temperature of the cell was slowly raised from 90°K to 195°K within a period of more than 2 hr. The composition of the gas phase was mass spectrometrically examined each 15 min. In Fig. 6 the number of molecules at a given time, N_t, divided by the number of molecules, N_E, in the state of equilibrium at 195°K is plotted against time and temperature. It is to be seen that the molecules of mass 29 which had been adsorbed on the surface precovered by $C^{12}O^{18}$ appear in the gas phase earlier than the molecules of the mass 30. We believe this result to be a proof for energetic heterogeneity of the film surface.

The above results with CO agree with those published by Schuit (*6*) and Gundry (*7*) who used H_2 and D_2 to study the heterogeneity of the surface. These authors also observed that with increasing tempera-

TABLE 1
ANALYSIS OF THE GAS PHASE AT 77°K TEMPERATURE OF ADSORPTION

T (°K)	Time	U Whole number of molecules × 10^{-16}			V Number of molecules in gas phase × 10^{-16}			Pressure (p, 10^{-3} mm Hg)	Ratio V/U (%)		
		$C^{12}O^{18}$	$C^{13}O^{16}$	$C^{12}O^{16}$	$C^{12}O^{18}$	$C^{13}O^{16}$	$C^{12}O^{16}$		$C^{12}O^{18}$	$C^{13}O^{16}$	$C^{12}O^{16}$
77°	t_a	21.0	48.0	91.7	0.08	0.38	20.2	1.4	0.4	0.8	22.1
	t_a	21.0	48.0	131.7	0.15	0.57	50.5	3.0	0.7	1.2	38.4
	t_a	21.0	48.0	170.5	0.18	0.67	79.6	4.9	0.9	1.4	46.7
	t_{60}	21.0	47.9	164.7	0.16	0.65	65.0	4.0	0.8	1.4	39.5
90°	t_a	21.0	47.9	164.7	0.18	0.82	65.5	4.6	0.9	1.7	39.8
	t_{60}	20.9	47.7	158.5	0.20	0.88	57.7	4.1	1.0	1.8	36.4
195°	t_a	19.9	44.1	136.9	4.2	10.5	33.5	5.3	21.1	23.8	24.5
	t_{45}	19.4	42.9	133.1	4.0	9.4	28.5	4.6	20.6	21.9	21.4
273°	t_a	19.4	42.9	133.1	5.3	12.1	32.8	8.4	27.3	28.2	24.6
	t_{45}	18.6	41.1	128.4	5.2	11.4	31.0	8.0	27.9	27.8	24.1

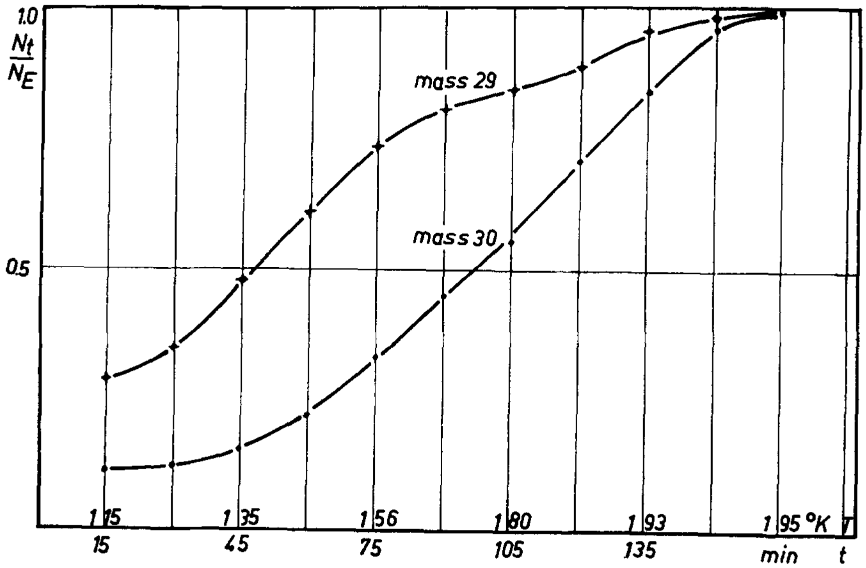

FIG. 6. Relative increase in concentration of the masses 29 (+) and 30 (○) in the gas phase as a function of temperature. Temperature of adsorption 77°K.

ture an increasing portion of the surface area took part in the equilibrium between adsorption phase and gas phase. Gundry (*7*) finds that 90% of the surface is "homogeneous" and inactive in low temperature exchange, 10% is "heterogeneous" and active. At the present state of our work we cannot deduce the shape of the energy distribution. Only further measurements can show whether the results with CO are consistent with the energy distribution proposed by Gundry.

Toya (*11*) recently made objections against the application of the "differential isotopic method" in determining the heterogeneity of metal films. He showed that it should be possible to decide between heterogeneity and homogeneity only when all surface sites were occupied and when all molecules were bound in the same manner. These objections especially are valid concerning the system hydrogen/nickel, where hydrogen is chemisorbed in two different species as is indicated by the change in resistance of evaporated nickel films with the adsorption of hydrogen (*12*). In the experiments described above the occupation of the surface sites was completed by the addition of $C^{12}O^{16}$. In this case the objections of Toya are not valid.

Adsorption at 293°K

The annealed Ni film was kept at a temperature of 273°K and covered at first with molecules of mass 30 to a coverage of 0.4×10^{15} molecules/cm^2, then with molecules of mass 29 to a coverage of 1.4×10^{15} molecules/cm^2 and lastly with molecules of mass 28 to a coverage of 2.2×10^{15} molecules/cm^2. Figure 7 shows that the increase in resistance is similar to that at 77°K shown in Fig. 5. At point B the equilibrium pressure was 2×10^{-8}, and at C, 1×10^{-7} mm Hg.

When a coverage of 2.2×10^{15} molecules/cm^2 was obtained the film was cooled to 77°K and additional carbon monoxide of mass 28 was added until a pressure of 2.7×10^{-3} mm Hg was measured. The composition of the gas phase is to be seen in Table 2. The meaning of the symbols is the same as in Table 1.

Just as in Table 1 the part of mass 30 and 29 in the gas phase is much smaller than that of mass 28. But there is not any difference in the figures for masses 30 and 29 either at 77° or at 90°K.

Also when the temperature is slowly raised to 195°K as in Fig. 6, the values N_t/N_E are equal for masses 30 and 29 at

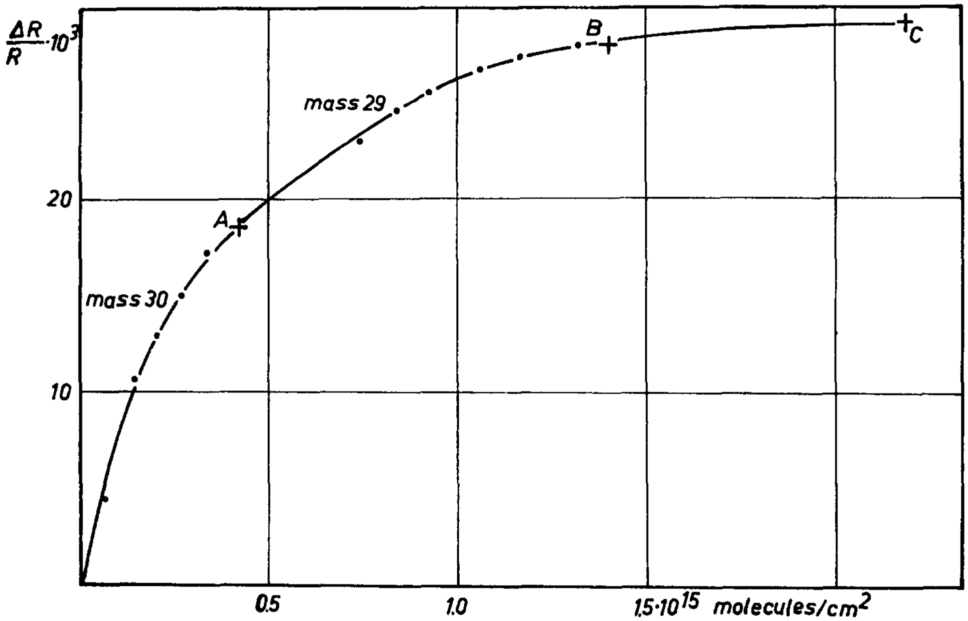

FIG. 7. Relative change in resistance as a function of coverage at $T = 273°K$. $C^{12}O^{18}$ was adsorbed until point A was reached and $C^{13}O^{16}$ until B was reached. $C^{12}O^{16}$ was adsorbed thereafter.

all times t as shown in Fig. 8. At 195°K the equilibrium between gas phase and adsorption phase is reached for all isotopic gases, as is shown by column V/U in Table 2.

This experiment shows the influence of the temperature on the mobility of adsorbed CO molecules. At low temperatures the molecules are fixed as soon as they have reached centers of high adsorption energy. At 273°K, however, the molecules are mobile enough to take part in a place change process. Therefore a surface heterogeneity can only be observed when the

TABLE 2

ANALYSIS OF THE GAS PHASE AT 273°K TEMPERATURE OF ADSORPTION

T (°K)	Time	U Whole number of molecules $\times 10^{-16}$			V Number of molecules in gas phase $\times 10^{-16}$			Pressure (p, 10^{-3} mm Hg)	Ratio V/U (%)		
		$C^{12}O^{18}$	$C^{13}O^{16}$	$C^{12}O^{16}$	$C^{12}O^{18}$	$C^{13}O^{16}$	$C^{12}O^{16}$		$C^{12}O^{18}$	$C^{13}O^{16}$	$C^{12}O^{16}$
77°	t_a	21.0	49.0	79.6	0.13	0.33	6.9	0.4	0.6	0.7	8.7
	t_a	21.0	49.0	119.3	0.30	0.74	34.5	2.1	1.4	1.5	28.9
	t_a	21.0	49.0	158.0	0.33	0.79	63.6	3.9	1.6	1.6	40.3
	t_{45}	20.8	48.6	154.8	0.27	0.58	44.5	2.7	1.3	1.2	28.8
90°	t_a	20.8	48.6	154.8	0.28	0.70	47.0	3.3	1.3	1.4	30.4
	t_a	20.8	48.6	187.6	0.28	0.68	71.2	5.0	1.3	1.4	38.0
	t_a	20.8	48.6	219.6	0.25	0.63	102	7.7	1.2	1.3	46.5
	t_{30}	20.7	48.3	215.5	0.24	0.63	90.5	6.5	1.2	1.3	42.1
195°	t_a	19.5	45.4	193.9	3.9	9.3	37.8	6.3	20.0	20.5	19.5
	t_{30}	19.2	44.7	191.0	3.4	8.3	33.0	5.5	17.7	18.6	17.3
273°	t_a	19.2	44.7	191.0	3.8	9.2	32.8	9.0	19.8	20.6	17.2
	t_{30}	18.8	43.8	187.7	3.7	9.0	31.9	8.7	19.7	20.4	17.0

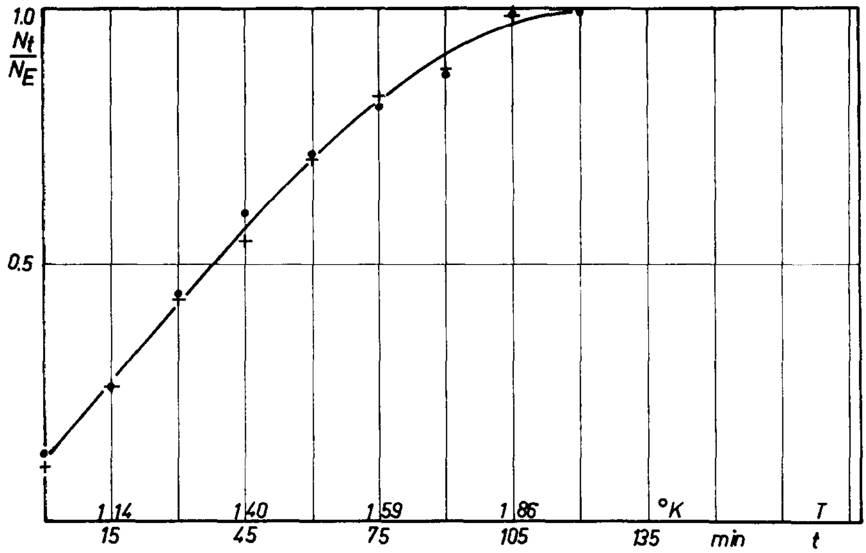

FIG. 8. Relative increase in concentration of masses 29 (+) and 30 (○) in the gas phase. Temperature of adsorption 273°K.

temperature of the adsorbing surface is low enough so that the molecules cannot leave the centers of high adsorption energy.

ACKNOWLEDGMENTS

The authors wish to thank the Deutsche Forschungsgemeinschaft and the Bundesministerium für Atomkernenergie und Wasserwirtschaft for their financial help.

REFERENCES

1. SUHRMANN, R., AND SCHULZ, K., *Z. physik. Chem. Neue Folge* **1,** 78 (1954); SUHRMANN, R., WEDLER, G., AND HEYNE, HJ., *Z. physik. Chem. Neue Folge* **22,** 336 (1959); SUHRMANN, R., OBER, H., AND WEDLER, G., *Z. physik. Chem. Neue Folge* **29,** 305 (1961).
2. WEDLER, G., unpublished data.
3. BRODSKY, A. E., "Isotopenchemie," p. 478. Akademie-Verlag, Berlin, 1961.
4. KUMMER, J. T., AND EMMETT, P. H., *J. Am. Chem. Soc.* **73,** 2886 (1951).
5. EISCHENS, R. P., *J. Am. Chem. Soc.* **74,** 6167 (1952).
6. SCHUIT, G. C. A., DEBOER, N. H., DORGELO, G. J. H., AND VAN REIJEN, L. L., *in* "Chemisorption" (Garner, W. E., ed.), p. 39. Butterworth, London, 1957; SCHUIT, G. C. A., AND VAN REIJEN, L. L., *Advances in Catalysis* **10,** 243 (1958).
7. GUNDRY, P. M., *in* "Actes du Deuxième Congrès International de Catalyse," p. 1083, Editions Technip, Paris, 1961.
8. BORESKOV, G. K., AND VASSILEVITCH, A. A., *in* "Actes du Deuxième Congrès International de Catalyse," p. 1095. Editions Technip, Paris, 1961.
9. GENTSCH, H., Thesis, Technische Hochschule Hannover, 1961.
10. GENTSCH, H., unpublished data.
11. TOYA, T., *J. Research Inst. Catalysis, Hokkaido Univ.* **9,** 134 (1961).
12. SUHRMANN, R., MIZUSHIMA, Y., HERMANN, A., AND WEDLER, G., *Z. physik. Chem. Neue Folge* **20,** 332 (1959).