Coprecipitated Adsorbent Gels

RICHARD G. CLARKE, RICHARD H. GROTH, and EDWARD J. DUZAK
Division of Research, University of Hartford, Hartford, Conn.

THE LITERATURE records studies of the adsorption of carbon dioxide on numerous dry absorbents including silica (*4*), charcoal (*24, 32, 39, 40*), Molecular Sieves (*20*), magnesia (*44*), alumina (*5, 34*), Ascarite (*38, 41, 45*), various metal oxides such as hopcalite (*1, 19*), manganese dioxide (*7*), cupric ferrite and chromite (*14, 18*), zinc chromite (*14, 18, 43*), zinc oxide (*33*), cupric oxide, chromic and ferric oxides (*1*), magnetite (*17*), oxides of titanium and tin (*29*), oxides of cerium and thallium (*29*), finely divided metals such as nickel, cobalt, iron, copper, platinum, and palladium (*16, 42*), on zeolite (*36*), solid sodium hydroxide and soda lime (*8, 14, 23*), and potassium superoxide (*25*).

All of these which are commercially important are subject to one or more of the following disadvantages: low efficiency, low capacity, requirement of considerable energy for regeneration of adsorbent, and preferential water vapor adsorption at the expense of carbon dioxide; the others have not been studied thoroughly.

No systematic survey of the many possible bivalent and trivalent metal oxide combinations has been made. In this investigation, such a survey was undertaken and the results obtained with iron and aluminum as the trivalent metals are reported.

The iron(III) oxide gels have in general high efficiency and capacity, are easily desorbed with input of small amounts of energy, and usually have a preference for carbon dioxide at the expense of water. Desorption at the nominal temperature of adsorption is referred to as "isothermal," although moderate cooling of the gel occurs.

Gels of this general type have been prepared by interaction of solutions of the metal salts with sodium carbonate or sodium hydroxide solutions *H* (*6, 9, 10, 15, 21, 28, 30, 31*). Other gels, prepared from aqueous media, have been desiccated by the use of certain organic solvents (*13, 35*). In this investigation, the gels have generally been made by coprecipitation of a solution of chlorides or nitrates of lithium, magnesium, calcium, barium, manganese(II), iron (II), cobalt, nickel, copper(II), cadmium, lead(II), silver, zinc, uranyl, vanadyl, mercury(I), and mercury(II) together with iron(III) or Al(III) by a potassium carbonate solution. The resulting precipitate is filtered and then washed successively with water, ethanol, and acetone. In this study, the proprietary solvent Synasol (Union Carbide Chemicals Co.), ethanol denatured by assorted ketones and hydrocarbons, was used. The gel is finally dried at 110° C. for 2 hours. Vacuum drying at 50° C. or less may be preferable. Generally, the gel consists of MO and Fe_2O_3 or MO and Al_2O_3. Carbonates initially formed in many cases have a transient existence and rapidly lose carbon dioxide before filtering. Carbonates of certain bivalent metals such as barium and calcium are stable, and in these cases, the gel probably contains MCO_3 and Fe_2O_3, and Al_2O_3.

PREPARATION

An example of the usual preparation follows [for preparation of $CoO:Fe_2O_3$, mole per cent Co(II) to Fe(III) 33.3 to 66.7].

A solution of cobalt(II) nitrate (0.1 mole, 29.1 grams) and iron (III) nitrate (0.2 mole, 80.8 grams) in water (400 ml.) and a solution of potassium carbonate (0.4 mole, 55.3 grams) in water (400 ml.) are prepared. With continuous stirring, the solution of cobalt(II) nitrate and iron(III) nitrate is then added to the potassium carbonate solution. Before addition is completed, evolution of carbon dioxide begins and governs the rate of addition. The gel precipitate is filtered using a Büchner funnel and water aspirator, redispersed twice in water (400 ml.), then in ethanol (600 ml.). After each dispersion, the slurry is filtered. This procedure will be referred to hereafter as the "Standard Preparation." In Al_2O_3-containing gels, further washing with acetone has been employed. In such cases, the treatment consisted of twice redispersing the gel in acetone (400 ml.).

The precipitate is allowed to dry in a borosilicate glass dish overnight. Residual solvent is removed by heating in an oven for 2 hours at 110° C. or by vacuum desiccation at lower temperature of Fe_2O_3-containing gels. Al_2O_3 gels were baked at 350° C. for 2 hours. Al_2O_3-containing gel samples permitted to stand for several weeks without baking were inferior adsorbents when baked (Table I). Sodium hydroxide may also be used as the precipitating agent, but in general the resultant gel is not a satisfactory carbon dioxide adsorbent.

Table I. Effect of Standing on Unbaked Gel

	CO_2 Adsorbed, Mg./G. Gel	
Sample	Original	After standing
65:35 $MgO:Al_2O_3$[a]	41.4	34.8
60:40 $CuO:Al_2O_3$[a]	31.7	22.9
75:25 $ZnO:Al_2O_3$[a]	34.3	25.6

[a] Samples prepared in standard way but not solvent desiccated.

In the preparation of gels containing mercury, acid was added to render the salts soluble, and was compensated for by addition of more carbonate. In the gels containing mercury and silver, decomposition occurred to some extent upon heating to 110° C. The vanadyl gels were made from soluble sulfate salts.

Effect of Certain Preparation Variables on Activity. Low temperature, excess of carbonate, slow addition of metal nitrates to carbonate, and additional water washing all improve the activity of Fe_2O_3-containing gels. This procedure is subsequently referred to as "Improved Preparation." Excessive washing by desiccating solvents is undesirable. Higher temperatures, either for starting solutions or in final drying of the gel, reduce activity (Tables II, III, and IV). Completion of the desiccation of a Fe_2O_3-containing gel by heating above 110° C. seriously diminishes specific surface.

The surface area of $MgO:Al_2O_3$ was widely varied within a given composition by changes in preparative technique (Table V). These results indicate that slight deficiency of potassium carbonate, slow addition, and baking for 2 hours at 350° C. definitely produce a better gel, and very cold or concentrated solutions are to be avoided.

The use of ammonium hydroxide as the precipitant results in a less adsorptive gel—$MgO:Al_2O_3$ 67:33 from K_2CO_3 adsorbed 26.4 mg. of CO_2 per gram of gel; $MgO:Al_2O_3$ 67:33 from NH_4OH adsorbed 11 mg. of CO_2 per gram (both measured by the static method).

Table II. Effect of Various Conditions in Preparation of Fe_2O_3 Gels

(Dynamic test conditions)

		Cycle					
		25° – 25° C.			0° – 25° C.		
Sample	Treatment	*A*	*D*	CO_2 %	*A*	*D*	CO_2 %
1.	Cold solutions; metal solution 9.5° C., carbonate solution, 16° C.	29	15	50	36.5	26.8	74
2.	Standard[a]	24.2	13.6	58	32.6	23.3	71
3.	Slow addition; metal ions added via buret with continuous stirring	25	12.7	50	38.2	26.0	68
4.	5% excess of carbonate[b]	33	16.2	50	42.6	26.4	60
5.	5% deficiency of carbonate	4	. . .	. . .	. . .	. . .	. . .
6.	Second wash, 400 ml. water	25	15	60	38.2	28.6	74
7.	Treatments listed for 1, 3, 4, 6	42.3	24.2	60	59.4	39.6	67

A = CO_2 adsorbed mg./gram gel.
D = CO_2 desorbed in vacuo at specified temperature, mg. / gram gel.

[a] Standard conditions. carbonate solution, temperature 30° C., metal, 20° C. Precipitated as quickly as possible.

[b] 10% Excess of carbonate gave about the sample results; a 15% excess of carbonate gave lower activity. Optimum results for this gel are obtained when the metal ions are added until the pH falls to 5. All samples were washed twice in acetone following the ethanol wash.

Table III. Solvent Desiccation of $CoO:Fe_2O_3$, 33.3:66.7[a]

Washing		Adsorption, 25° C.		Adsorption, 0° C.	
Ethanol	Acetone	*A*	*D*	*A*	*D*
1	2	40.9	21.1	50.6	29.6
1	0	52.8	26.4	88	55
2	0	37.4	22	50.6	33
1	1	43.1	19.4	57.2	30.8
0	1	38.7	18	59.4	34.7
0	2	35.2	13.2	61.6	33.9

A = CO_2 adsorbed mg./gram gel
D = CO_2 desorbed mg./gram gel

[a] Heated for 3 hours, 110° C. Improved preparation, slow mixing of cold solutions . Desorbed 25° C.

Table V. Effect of Variation in Preparative Technique

($MgO:Al_2O_3$ 65:35)[a]

Condition	CO_2 Adsorbed, Mg./G. Gel[b]
Standard preparation	30
Chilled solutions	26.5
Diluted solutions	27.7
Concentrated solutions	22.0
5% excess K_2CO_3	32.6
5% deficiency K_2CO_3	41.4
Reverse order of mixing	35.6
Na_2CO_3	33.8
Slow addition	41.4
5% deficiency of K_2CO_3	
Bake 1 hour at 250° C.	15.9
Bake 2 hours at 250° C.	18.0

[a] Not solvent desiccated.
[b] Determined by static method.

Table IV. Effect of Heating on Gel

A. $MgOFe_2O_3$[a] 70:30

Drying temp., ° C.	110	250	350	450	600
Duration of heating, hours	12	3.5	2	1	0.5
CO_2 adsorbed, mg./gram gel	27.5	18.9	19.8	19.8	16.7

B. $CoOFe_2O_3$[b]

		CO_2, Mg./G. Gel.			
Composition	Time, Hours	Adsorb, 25° C.	Desorb	Adsorb, 0° C.	Desorb
33/67	1	57.2	30.8	83.6	59.4
	2	55	28.6	72.6	48.4
	3	52.8	24.6	70.4	44
	0.5[c]	22	11	37.4	28.6
5/95	0	61.7	30.8	101.2	66
	1	35.2	22	59.4	46.2

[a] Air dried, adsorption from static atmosphere of pure CO_2; standard preparation, washed twice with acetone.
[b] Improved preparation, slow mixing of cold solution; air dried followed by indicated oven drying at 110° C.
[c] Baked at 350° C.

The use of organic solvents for desiccation (*13, 35*) also results in a more adsorptive gel—$MgO:Al_2O_3$, 15.5 mg. of CO_2 adsorbed per gram and desorbed under isothermal conditions 4 mg. of CO_2 per gram for untreated gel as compared to 26.8 mg. of CO_2 adsorbed and 5.8 mg. of CO_2 desorbed per gram for solvent desiccated gel (both measured by the dynamic method).

CHEMICAL ANALYSIS

The compositions given are based on the mole ratio of M^{+2} to Fe^{+3} or Al^{+3} in the metal ion solution as prepared for precipitation; the actual composition deviates from these values. This deviation results from incomplete precipitation due to low pH and to formation of carbonates or bicarbonates. Also, air oxidation would affect the nature of the $FeO:Fe_2O_3$ and $CoO:Fe_2O_3$ mixtures.

The following analytical results were obtained:

Nickel Oxide–Iron Oxide.

	Composition Based on Starting Materials	Analysis
Ni(II):Fe(III)	5:95	2.5:97.5
	10:90	5.5:94.5
	15:85	9:91
	20:80	13.5:86.5
	25:75	18:82
	30:70	21.7:78.3

Nickel was determined by dimethylglyoxime precipitation(*3*). The pH of these samples at the time of precipitation increased from 4.9 to 6.1 in this series. The approximate pH for complete precipitation of Ni(II) is 6.6 and of Fe(III) is 2.2 (*27*).

Ferrous Oxide–Ferric Oxide. In five samples ranging from starting composition 20:80 Fe(II):Fe(III) to 80:20. no Fe(II) was detected by dichromate titration of the samples dissolved in HCl by the usual procedure. In the case of $FeO:Fe_2O_3$, 33.3:66.7, after the second dispersion in water, a proximate analysis of the sample showed 13:87, Fe(II): Fe(III); after the ethanol wash, 7.7:92.3 analysis; after two washings in acetone, 1.45:98.55; and after 24 hours of air drying, no Fe(II).

Manganous Oxide–Iron Oxide.

	Composition Based on Starting Material	Analysis
Mn(II):Fe(III)	5:95	2.3:97.7
	10:90	3.8:96.2
	20:80	10.1:89.9
	33:67	20.9:79.1
	40:60	27.6:72.4
	50:50	46.7:53.3
	60:40	51.2:48.8
	70:30	64.2:35.6
	80:20	78.4:21.6

The Fe(III) was determined by the dichromate titration method and Mn(II) colorimetrically after oxidation to MnO_4^- and with Fe(III) masked by use of H_3PO_4(*46*). The pH for the 33:67 sample was 6.5 and the pH for complete precipitation for Mn(II) is 8.8 (*24*).

Cobalt Oxide–Iron Oxide.

	Composition Based on Starting Material	Analysis
Co(II):Fe(III)	5:95	0.6:99.4
	20:80	11:89
	33:67	20.5:79.5
	50:50	41:59
	70:30	67.5:32.5

The Fe(III) after separation from Co(II) with use of NH_4OH was determined by dichromate titration. The Co(II) was determined both colorimetrically with nitroso-R-salt (*22*) and by precipitation with 1-nitroso-2-naphthol (*12*). Because of air oxidation in basic media some cobalt is undoubtedly in the form of Co(III). The pH ranged from 5.1 for the 5:95 to 6.3 for the 33:67 samples and the pH for complete precipitation is 6.6 for Co(II) (*26*).

Copper Oxide–Iron Oxide.

	Composition Based on Starting Material	Analysis
Cu(II):Fe(III)	5:95	4.6:95.4
	10:90	9.3:90.7
	23:77	21.3:78.7
	33:67	37.7:62.3
	50:50	56.4:43.6
	60:40	64:36
	70:30	79:21

Both Cu(II) and Fe(III) were determined by iodometric titration (*2*). The pH ranged from 4.7 for the 5:95 sample to 5.4 for the 33:67 sample and the pH for complete precipitation is 5.1 for Cu(II) (*27*).

Magnesium Oxide–Aluminum Oxide. In the case of $MgO:Al_2O_3$, the pH for the gel slurry at its first precipitation ranged from 5.8 to 9.1 for samples of starting composition Mg^{+2} to Al^{+3} ranging from 10:90 to 80:20 and the pH for complete precipitation of Mg^{+2} is 10.5 (*27*). Analysis of these samples for Mg^{+2} and Al^{+3} by (ethylenedinitrilo)tetraacetic acid methods (*26*) gave the following results:

	Composition Based on Starting Material	Analysis
Mg(II):Al(III)	10:90	1.1:98.9
	25:75	7.3:92.7
	33.3:66.7	12.9:87.1
	40:60	19.2:80.8
	60:40	32.4:67.6
	80:20	61.0:39.0

PROPERTIES

Carbon Dioxide Adsorption and Water Adsorption. Adsorption of carbon dioxide by the gels was studied in dynamic and static systems. In the dynamic system, 100% carbon dioxide or a dilute solution of carbon dioxide in dry air is passed for 20 minutes through a train consisting of a tube of the gel and a tube of magnesium perchlorate. The gain in weight of the gel plus the gain in the magnesium perchlorate tube represents the weight of carbon dioxide adsorbed. Desorption is effected by use of a vacuum pump (evacuating the train to 75 microns pressure), drawing off the carbon dioxide from the gel through the magnesium perchlorate tube for 20 minutes. The loss in weight of the gel, corrected by the gain in the magnesium perchlorate, represents the weight of carbon dioxide desorbed. Cycles were run in which adsorption and desorption were effected at room temperature (25° C.), also with adsorption at 0° and desorption at 25° C.

In the static system, the weighed gel sample was placed in an atmosphere of 100% carbon dioxide and reweighed after 30 minutes (Table VI).

Water adsorption was measured by placing the gel sample for 24 hours in an atmosphere of 50% relative humidity (RH). The sample was then placed in a tube and desorbed at the pump. Water desorbed was taken up by a magnesium perchlorate tube.

Illustrations of some of the satisfactory, reversible carbon dioxide and water adsorbers are given in Table VII. Adsorption from dilute solutions of carbon dioxide are compared with 100% carbon dioxide (Table VIII). The values compare well with predictions based on the adsorption isotherms.

Surface Area. Methyl red dye in dry benzene has been used (*37*) to measure silica surfaces and it measures only the hydroxylated surface. Table IX gives some comparative results obtained for various gel surfaces measured with methyl red and carbon dioxide. The surface of the iron oxide–containing gels is probably not fully hydrated. The surface area of the gels was computed by carbon dioxide adsorption assuming a monomolecular layer of CO_2. Only the major cross-sectional area of the molecule (taken to be 17 sq. A.) was considered in the calculations. If the carbon dioxide molecule lies flat and is permitted free rotation, the surface required per molecule is about twice as great.

Gel Esters. Iler (*11*) has prepared esters of silica gels which are strongly hydrophobic. In this investigation, esterified gel samples have been prepared by the use of *n*-amyl alcohol with an Al_2O_3-base gel.

Table VI. Static Adsorption of CO_2

$MO:Al_2O_3$, 33.3:66.7[a,b]		$MO:Fe_2O_3$, 33.3:66.7[a,c]	
Gel	CO_2 adsorbed, mg./g. gel	Gel	CO_2 adsorbed, mg./g. gel
Cu	23.8	Cu	35.2
Zn	37.8	Zn	33
Fe(II)	38.3	Fe(II)	27.7
Mg	36.5	Mg	23.8
Ca	25.5	Ca	22.9
Li[d]	47.5	Li[d]	25.6
Ni	35.6	Ni	37
Mn	29.0	Mn	35.6
Hg(I)	4.8	Hg(I)	4.8
Hg(II)	0	Hg(II)	3.1
Pb(II)	22.9	Pb(II)	23.8
Cd	22.9	Cd	23.8
Ba	22.9	Ba	19.4
Ag	15.0	Ag	4.0
Sn(II)	8.8	Co(II)	29
Uranyl	14.5	UO_2	15.8
Vanadyl	7.9	VO_2	15.8

[a] Standard preparation, washed twice with acetone.
[b] Dried for 2 hours at 350° C.
[c] Dried for 2 hours at 110° C.
[d] $Li_2O:Fe_2O_3$, 50:50.

In the case of n-amyl alcohol, $MgO:Al_2O_3$, 33:67, solvent desiccated, was refluxed for 6 hours with the alcohol. The slurry was then filtered, and washed with ethanol and acetone. The product takes up 3% of its weight in water from a 50% RH atmosphere as compared to 34% of its weight for the starting material, thus indicating a change from hydrophilic to hydrophobic characteristics and a conversion to the ester. The water taken up by the ester gel is 100% desorbed on evacuation at room temperature. The original sample, under similar conditions, still retains 30% by weight of water. Carbon dioxide adsorption by the ester gel is 18.9 mg. of CO_2 per gram and desorption is 18.9 mg. of CO_2 per gram as compared to 29 and 5.3 for the original dry material (dynamic measurement).

The alcohol moiety in the ester gel is removed by heating to 500° C. for 1 hour. This de-esterified gel adsorbs 86 mg. of CO_2 per gram gel and desorbs 23.8 mg. of CO_2 per gram (dynamic conditions), and picks up 23% of its weight in water at 50% RH. This hydrated, de-esterified gel adsorbs 145.3 mg. of CO_2 per gram and desorbs 22.9 mg. of CO_2 per gram, as compared to 149.8 and 15.4 for the original hydrated gel (dynamic measurement).

Table VII. Adsorption by Fe_2O_3-Containing Gels

A. Water and Carbon Dioxide[a]

Composition, Mole % of Metals	85:15	70:30	55:45
H_2O adsorbed, %, 50% RH	4.0	8.8	3.5
CO_2 adsorbed, mg./g. gel on hydrated gel	17.6	105.6	30.8
CO_2 desorbed, mg./g. gel isothermal	4.4	13.6	8.4

B. Carbon Dioxide[b]

Components	CO_2, Mg. G. Gel			
	Adsorbed, 0° C.	Desorbed	Adsorbed, 25° C.	Desorbed
$NiO:Fe_2O_3$	52.8	39.6	39.6	26.4
$MnO:Fe_2O_3$	52.8	38.7	34.7	22
$CoO:Fe_2O_3$	59.4	36.5	41.3	18
$CuO:Fe_2O_3$	35.2	25.2	22.4	22

[a] Adsorption by $MgO:Fe_2O_3$, standard preparation, washed twice with acetone, dried for 2 hours at 110° C.

[b] Adsorption of various $MO:Fe_2O_3$ gels, 33.3:66.7 composition; desorption at 10^{-4} atm. at 25° C. Improved preparation, washed twice with acetone, dried for 2 hours at 110° C.

Table VIII. Adsorption from 0.5% CO_2 in Air at 25° C.[a]

Gel	Composition	CO_2 Adsorbed, Mg./G. Gel			
				CO_2, 0.005 Atm.	
		CO_2, 1.0 atm.	CO_2, 10^{-4} atm.	Obsd.	Predicted from isotherm
$CoOFe_2O_3$	5/95	121	77.4	93.3	90.8
$CoOFe_2O_3$	33/67	114.3	92.3	102.8	102.0
$CuOFe_2O_3$	33/67	70.4	47.5	55.4	54.5
$CuOFe_2O_3$	5/95	79.2	52.8	61.6	60.7
$NiOFe_2O_3$	5/95	85.8	58.5	69.1	67.8
$CoOMnOFe_2O_3$	5/5/90	59	30.8	39.6	40.4
$CoONiOFe_2O_3$	5/5/90	50.6	15.4	28.6	30.8
Fe_2O_3		63.7	33.0	11.9	12.3

[a] Improved preparation, slow mixing of cold solutions, desiccated in vacuo at 50° C.

Attempts to prepare esters of iron oxide gels by this procedure have been unsuccessful.

Nature of Adsorption. A clear-cut division of the properties of the adsorbed CO_2 has been observed. Many freshly prepared gels containing iron oxide, especially those that are unusually hydrophobic (low water content), display substantially 100% desorption under conditions that are nominally isothermal. As the gel sample is put through a number of adsorption-desorption cycles with desorption pressure above 10^{-4} atm., the specific surface increases, and the per cent of isothermally desorbable CO_2 falls. Cycling with desorption pressures of the order of 10^{-5} atm. tends to prevent permanent adsorption.

If much water is present in the virgin preparation, it is gradually removed by cycling, most of it in the adsorption leg of the cycle. It is not swept out by CO_2-free air, nor removed in vacuo in the absence of CO_2. As water is removed, nondesorbable CO_2 is taken up by the gel, essentially milligram for milligram. If a gel containing a few per cent of water is heated at 50° to 100° C. in a stream of CO_2 most of the water is removed, and is replaced by CO_2 that is nondesorbable in vacuo at room temperature.

The residual water on the gel is probably chemisorbed. Two hours of baking at 110° C. is usually adequate for the removal of loosely held water. Chemisorbed water appears to be replaced by chemisorbed CO_2.

The isothermally reversible CO_2 appears to be held by Van der Waals forces in physical adsorption. Very little heat is given off during adsorption, and the sample is not cooled appreciably during vacuum desorption. The measured heat of physical adsorption of CO_2 on a gel that assayed 99.8% Fe_2O_3 is 3.0 ± 0.3 kcal. per mole of CO_2. The rate constants for adsorption and desorption are probably very high. The constant for adsorption is independent of pressure between 1 and 0.005 atm. of CO_2, so the rate-determining process is possibly the diffusion of CO_2 into and out of the gel particle, rather than the mechanics of adsorption. Attempts to determine the adsorption rate constant have not been successful, since it is technically not a simple matter to flood a gel sample with CO_2, and then remove the unadsorbed portion, in seconds.

The desorption rate constant for iron oxide base gels was measured at 500, 75, and 10 microns desorption pressure, and varied inversely as the logarithm of the pressure, or directly as the log volume of gas pumped. Thus, the rate in desorption in the apparatus used is determined by the pumping speed. The entire study was associated with a space craft design problem, and the apparatus was in rough similitude to the envisioned equipment. An apparatus that would make some other

Table IX. Specific Surface of Fe_2O_3-Containing Gels[a]

Sample	Treatment	CO_2 Adsorbed, Mg./G. Gel	S CO_2, Sq. M./G.	$S_{Methyl\ Red}$, Sq. M./G.
$FeO:Fe_2O_3$ 33:67	Dried, 4 hours, 110° C.	30.8	70	125
$MgO:Fe_2O_3$ 70:30	Hydrated, overnight at 50% RH	105.5	240	276
$MgO:Fe_2O_3$ 70:30	Dried, overnight, 110° C.	35.2	80	227
$MnO:Fe_2O_3$ 33:67	Hydrated, overnight at 50% RH	63.7	145	175
$MnO:Fe_2O_3$ 33:67	Dried, overnight, 110° C.	37.8	86	>15
$MgO:Al_2O_3$ 33:67	Hydrated, overnight at 50% RH	176	400	800
$MgO:Al_2O_3$ 33:67	Hydrated, overnight at 50% RH and then heated 1 hour, 100° C.	33	75	500

[a] Standard preparation, washed twice with acetone.

parameter of the desorption process rate-determining could be designed, but this was beyond the scope of the study.

The Al_2O_3-base gels show extensive chemisorption of water and carbon dioxide, with limited additional physical adsorption, whereas the iron oxide gels tend to adsorb CO_2 physically. In most instances, water adsorption by Al_2O_3 gels is less reversible isothermally than that by Fe_2O_3 gels.

Thermochemical measurements have contributed to the understanding of the adsorption process in the Al_2O_3-base gels. Heat of adsorption of the first few per cent of water to be taken up by $MgO:Al_2O_3$, 33:67 gel was 18 kcal. per mole, comparable to the heat of hydration of MgO and Al_2O_3 by water vapor, 15 and 14 kcal. per mole, respectively.

In the calorimetric measurements it was necessary to employ a system with gas flow through the sample. The difficulty of obtaining quantitative transfer of the heat of reaction of the calorimeter from the gas stream would be expected to diminish the accuracy of the results. Duplicate measurements were of reasonable precision, ±10%, but accuracy might have been no better than ±20%. Heats of adsorption of CO_2 are probably more accurate than heats of hydration, since the total gas flow was smaller in the measurement of the former.

On the other hand, the heat of hydration of $Li_2O:Al_2O_3$, 50:50, was found to be 10 kcal. per mole, comparable to the latent heat of vaporization of water, rather than 32 kcal. per mole, the hydration heat of lithium oxide. The heat of hydration of $BaO:Al_2O_3$, 33:67, was 13 kcal. per mole, with the heat of hydration of BaO, 35 kcal. per mole. Clearly, the hydration of these samples was of the nature of physical adsorption. In both instances, water adsorption is extensively reversible isothermally, suggestive of the physical process.

All Al_2O_3-containing samples were prepared for calorimetry by baking for 2 hours at 350° C. immediately before testing. Application of Nernst's approximation of the heat theorem to magnesium, lithium, and barium hydrates indicates that only the magnesium compound will lose water extensively at 350° C. Thus, the samples of $Li_2O:Al_2O_3$ 50:50 and $BaO:Al_2O_3$ 33:67 may never have been fully freed of the water used in preparation, so that at least the surface lithium and barium ions were covered by a hydrate monolayer when the heat of adsorption of water was measured.

By comparison, the heats of carbonate adsorption were decisively clear. They are, well within the probable experimental error, equal to the heats of carbonate formation from the respective oxides and CO_2 (Table X). In carbonate adsorption calorimetry, the sample was desorbed in vacuo after adsorption in the calorimeter, and CO_2 lost by isothermal desorption was deducted from the total adsorbed, on the ground that the heat of CO_2 physical adsorption is very small compared to that of chemisorption; hence the measured heat of reaction should be related to the weight of the isothermally nondesorbable CO_2 only.

The authors conclude that water adsorbed on the extensively dehydrated $MgO:Al_2O_3$, 33:67 gel went into the monolayer as the hydrate; water adsorbed on $Li_2O:Al_2O_3$, 50:50 and on $BaO:Al_2O_3$, 33:67 gels went into a higher layer, or as a monolayer hydrating the aluminum oxide centers of the surface, since the lithium and barium center had probably never been dehydrated from the original preparation; and chemisorbed CO_2 on $MgO:Al_2O_3$, $BaO:Al_2O_3$, and $Li_2O:Al_2O_3$ gels went to the surface as a monolayer of carbonate ion.

Table X. Heat of Adsorption of Al_2O_3-Containing Gels

ΔH, Kcal./Mole	$MgO:Al_2O_3$	$Li_2O:Al_2O_3$	$BaO:Al_2O_3$
Water adsorption on gel	18	10	13
Oxide hydration[a]	15	32	35
CO_2 adsorption on gel	26	52	58
Carbonate formation from oxide[a]	27	55	64

[a] Computed from data, International Critical Tables, Hydration by H_2O vapor.

No attempt was made to measure the heat of adsorption of the fraction of CO_2 physically adsorbed in Al_2O_3-base gels. It is probably of the order of the 3 kcal. per mole measured on ferric oxide.

Adsorption Isotherm. If a gel of a transitional bivalent metal oxide and iron oxide is prepared without heating in the preliminary drying stage, and is finally desiccated in vacuo at 50° C. the resulting gel tends to cycle without chemisorption.

The isotherm for such a substance indicates that the adsorption rate constant is independent of pressure, but the capacity of the material for CO_2 is proportional to the logarithm of the pressure. Typical of these materials are $CoO:Fe_2O_3$ and $NiO:Fe_2O_3$ gels (Figures 1 and 2). For comparison, a commercial material (Linde Molecular Sieve 5A) that is a Langmuir adsorbent displays a very differently shaped isotherm (Figure 3).

$CoO:Fe_2O_3$ was carried through 100 cycles of adsorption and desorption after heating to 50° C. in the presence of CO_2. The chemisorption process was triggered by the treatment, for the growth of nondesorbable CO_2 with

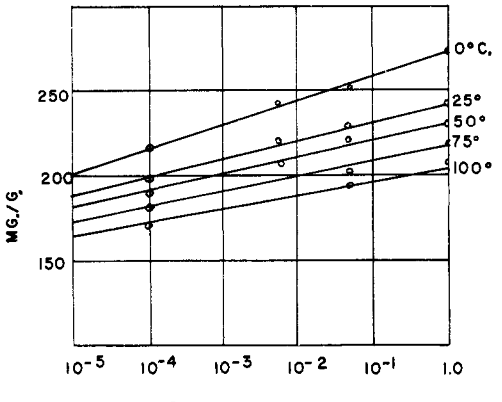

Figure 1. Adsorption isotherms for CO_2 on $CoO:Fe_2O_3$, 5:95 gel, maximum chemisorption

Desorption 20 minutes at 10^{-4} atm., nonequilibrium; all isotherms intersect at 10^{-9} atm.

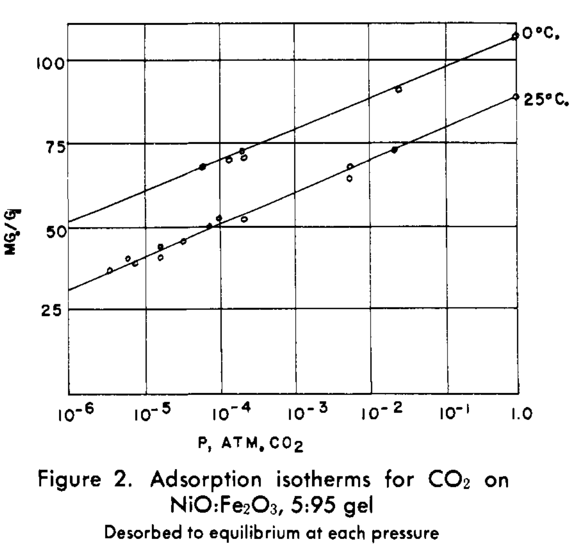

Figure 2. Adsorption isotherms for CO_2 on $NiO:Fe_2O_3$, 5:95 gel

Desorbed to equilibrium at each pressure

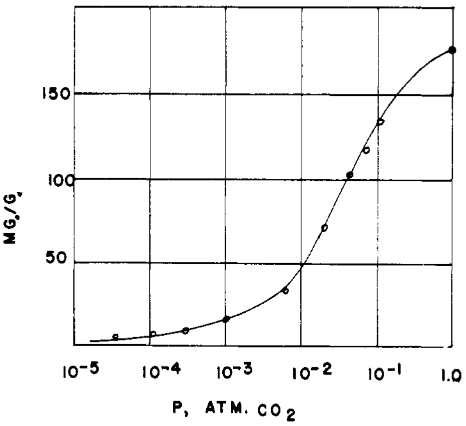

Figure 3. Isotherm at 25° C. on a Langmuir adsorbent (Linde Molecular Sieve 5A)

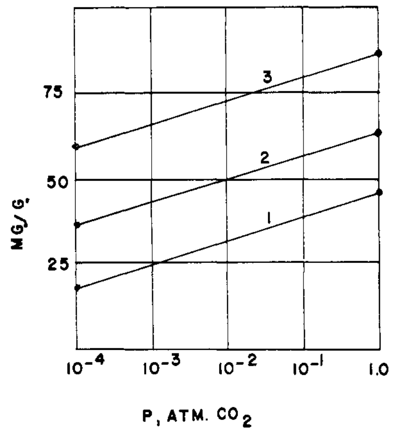

Figure 4. Adsorption isotherms of a single sample on $CoO:Fe_2O_3$, 5:95 gel

1. After 20 cycles, not heated with CO_2
2. Same + three cycles at 50° C. + three cycles at 25° C.
3. Treatment 2 + 10 cycles at 25° C.

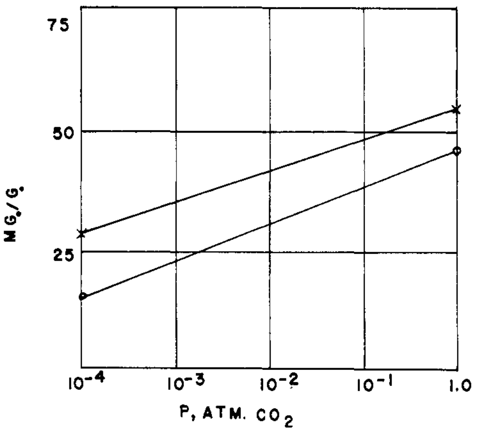

Figure 5. Adsorption isotherms on $CoO:Fe_2O_3$, 5:95 gel not heated in presence of CO_2

o———o 10 cycles x———x 50 cycles

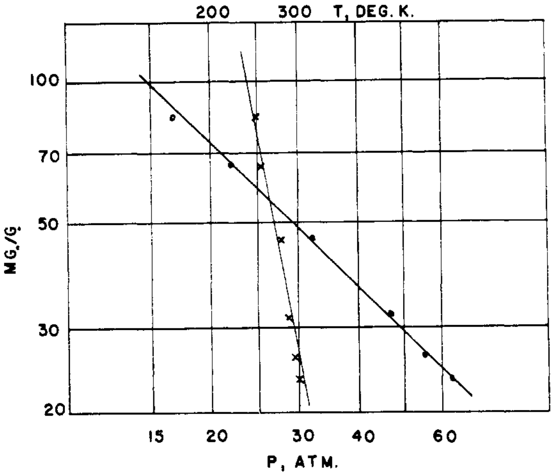

Figure 6. Effect of temperature on adsorption of CO_2 on $CoO:Fe_2O_3$, 5:95 gel, improved preparation

x———x Temp., ° K o———o Vapor pressure CO_2

cycling is clearly evident (Figure 4). A sample of the same material that was never heated in contact with CO_2 does not show growth of chemisorption to the same extent (Figure 5).

An attempt was made to determine the nature of the reversibly adsorbed CO_2 layer. Adsorption below the critical temperature is inversely proportional to the vapor pressure of CO_2, rather than to the temperature itself. Data are plotted (Figure 6) to logarithmic scales, so the inverse relationship is indicated by a slope of -1 for the vapor pressure curve. The temperature-adsorption curve deviates strongly from -1 slope. Thus, the liquid phase of CO_2 or a film analogous in structure to the liquid, must be present. Above the critical temperature, adsorption is temperature dependent, so the adsorbed layer is presumably in a condition analogous to a gas.

Preliminary investigation of one of the $MgO:Fe_2O_3$, 70:30, preparations indicates that at 200° C. adsorption is still as strong as at 25° C., although the desorption rate slows remarkably at 200° C. Computation from rate constants by Nernst's approximate solution of the heat theorem indicates a ΔH of 22 kcal. per mole, so chemisorption is apparently dominant at 200° C.

It is not easy to detect heating upon adsorption of water vapor, since the solution of water is necessarily dilute in air at 25° C., but upon vacuum desorption a hydrated gel cools markedly, indicative of a somewhat higher heat of adsorption than is observed with CO_2.

An anomaly is observed in hydrophilic gels. Carbon dioxide (100% atm.) drives water so vigorously from the hydrated gels that steam forms in the empty parts of the adsorption tube, and the apparatus heats strongly. Usually, a strongly hydrated gel will take up three or four times as much CO_2 as it will adsorb when dry, but it will not desorb it readily in an isothermal cycle. This would suggest that chemisorbed water is replaced by chemisorbed CO_2. The weight balance indicates that the exchange is approximately one molecule of CO_2 for two of water, a reasonable figure, if CO_2 maintains free rotation space on the surface.

CONCLUSION

Appreciable differences in adsorptive capacity toward CO_2 have been noted between gels based on Fe_2O_3 and Al_2O_3, both with regard to the nature of the bivalent metal involved and to the percentage composition of the gel with respect to mole ratio of bivalent to trivalent metal.

Tables XI and XII show the variation of CO_2 adsorbed and desorbed for various gels. Mole fractions of bivalent

Table XI. Variation with Composition of Iron Oxide-Containing Gels in CO_2 Adsorption

		Adsorption Temperature, ° C.			
		0		25	
Component	Composition	*A*	*D*	*A*	*D*
$CoO:Fe_2O_3$[a]	35:65	35.2	22	26.8	13.2
	30:70	50.6	26.4	38.7	14.1
	25:75	48.4	33	36.5	19.8
	20:80	61.7	33	35.2	18.5
	15:85	68.2	38.6	50.6	22
	10:90	55	37.4	40.5	22
	5:95	74.8	46.2	52.8	22
	0:100	79.3	38.6	52.8	22
$CuO:Fe_2O_3$	35:65	44	27.3	32.5	17.6
	30:70	37.4	26.4	29.4	19.3
	25:75	57.2	31.6	36.9	18.5
	20:80	50.6	33	37.8	20.7
	15:85	61.7	38.3	44	22
	10:90	55	35.2	38.6	20.2
	5:95	66	41.8	48.4	24.2

A = CO_2 adsorbed mg./gram gel.
D = CO_2 desorbed mg./gram gel.

[a] Preparations using 5% excess K_2CO_3 as precipitant (low temperature, double water wash, slow addition).

metal ion in trivalent metal ion represent starting mole fractions used. True mole fractions vary because of solubility factors: With $FeO:Fe_2O_3$ the oxidation of iron(II) in air results in a final preparation consisting entirely of Fe_2O_3, although properties of the gel are a function of the starting composition.

Table XIII shows the variation of CO_2 adsorption and desorption for gels with the bivalent metal. Data for the "spinel composition" (33:67) for $MO:Fe_2O_3$ and 50:50 for $M_2O:Fe_2O_3$ are given.

$CoO:Fe_2O_3$, 5:95 was found to be the best of several effective and useful reversible CO_2 adsorbents. It desorbs and adsorbs reversibly (a total of 66 mg. of CO_2 per gram of gel) using a cycle of 0° C. for adsorption and 25° C. for desorption. It does not exhibit preferential adsorption of, or poisoning by water, and is regenerable with small energy considerations. It is reversible to the extent of about 65% of the initial adsorption. The best pure Fe_2O_3 gel showed a reversible capacity of 39.6 mg. of CO_2 per gram of gel. The best pure Al_2O_3 preparation had a reversible capacity of 16.3 mg. of CO_2 per gram of gel (hydrated) and 11 mg. of CO_2 per gram of gel (dry). Linde Molecular Sieve 5A and Davison silica gel both preferentially adsorb H_2O and H_2O displaces CO_2 from the adsorbent.

For adsorption at 1-atm. partial pressure of CO_2, and desorption at 10^{-4} atm., partial pressure, dry Linde Molecular Sieves are distinctly superior to our best gel. However, because of the differing character of the isotherms, the $CoO:Fe_2O_3$, 5:95, gel is equal in cycling performance to the dry Sieve at 0.005 atm., partial pressure in adsorption and 10^{-4} atm. in desorption. The Sieve loses its effectiveness as it accumulates H_2O, and our gel is not affected by water.

Table XII. $MgO:Al_2O_3$ Gel[a] Properties in Dynamic Testing

Conditions	65/35		60/40		40/60		33/67		23/77		10/90		5/95		2/98		0/100	
RH	50	0	50	0	50	0	50	0	50	0	50	0	50	0	50	0	50	0
Adsorbed CO_2, mg./g. gel	106	26	106	16	121	21	150	29	125	33	84	37	53	31	44	22	33	23
Desorbed CO_2, mg./g. gel	14	5.7	13	4.8	13	5.3	14	5.3	14	5.3	18	7.5	16	12	14	7.9	16	11
Adsorbed H_2O, %	30	0	29	0	31	0	34	0	25	0	22	0	19	0	17	0	16	0

[a] Precipitated by K_2CO_3, solvent desiccated, baked for 2 hours at 350° C.

Table XIII. Dynamic Adsorption of CO_2[a]

($MO:Fe_2O_3$, 33.3:66.7 Gels; Dried 2 Hours, 110° C.)

Conditions	Manganese		Iron		Cobalt		Nickel		Copper		Zinc		Silver	
RH	50	0	50	0	50	0	50	0	50	0	50	0	50	0
A	64	37	53	46	57	30	44	34	62	38	53	34	26	13
D	15	22	15	22	12	13	13	14	30	17	13	13	6.6	8.8
Adsorbed H_2O, %	7	0	11	0	9	0	10	0	9	0	10	0	7	0

Conditions	Magnesium		Calcium		Barium		Lithium[b]	Cadmium	Mercury(II)	Lead	Mercury(I)	Uranyl	Vanadyl
RH	50	0	50	0	50	0	0	0	0	0	0	0	0
A	17	22	38	26	40	22	30	21	19	25	8.4	11	4.4
D	5.7	8.8	10	10	7.9	7.0	18	11	9.2	11	2.6	5.3	...
Adsorbed H_2O, %	7	0	10	0	7.5	0	0	0	0	0	0	0	0

($MO:Al_2O_3$, 33.3:66.7 Gels; Dried 2 Hours, 350° C.)

Conditions	Manganese		Iron(II)		Cobalt		Nickel		Copper		Zinc	
RH	50	0	50	0	50	0	50	0	50	0	50	0
A	51	28	62	25	64	29	88	35	29	22	64	28
D	11	7.0	11	8.4	15	7.5	20	7.9	5.7	10	12	6.6
Adsorbed H_2O, %	16	0	14	0	25	0	25	0	12	0	19	0

Conditions	Magnesium		Calcium		Barium		Lithium[c]		Cadmium		Mercury(II)
RH	50	0	50	0	50	0	50	0	50	0	0
A	150	29	70	28	75	18	128	45	73	19	7.9
D	15	5.3	10	4.0	10	2.7	26	5.7	12	6.6	2.2
Adsorbed H_2O, %	34	0	12	0	21	0	37	0	17	0	0

Conditions	Silver		Mercury(I)	Tin(II)	Lead(II)		Uranyl	Vanadyl
RH	50	0	0	0	50	0	0	0
A	19	5.3	12	0.9	41	19	3.5	2.2
D	7.9	3.5	4.4	0	6.2	5.3	0	0
Adsorbed H_2O, %	10	0	0	0	8	0	0	0

[a] Data from Survey set; standard preparation, washed twice with acetone. Desorption at 4 mm. pressure, 25° C. Adsorption at 25° C. Hydration at 50% RH over wet magnesium hydrate crystals, nominal temperature 27° C.

[b] $Li_2O:Fe_2O_3$, 50:50.

[c] $Li_2O:Al_2O_3$, 50:50.

RH = % relative humidity; *A* = CO_2 adsorbed mg./g. gel; *D* = CO_2 desorbed mg./g. gel.

LITERATURE CITED

(1) Benton, A.F., *J. Am. Chem. Soc.* **45**, 887-900 (1923).
(2) Brasted, R.C., *Anal. Chem.* **24**, 1040 (1952).
(3) Brunck, O., *Z. angew. Chem.* **20**, 834, 1844 (1907).
(4) Burtt, B.P., Kurbatov, J.D., *J. Am. Chem. Soc.* **70**, 2278-82 (1948).
(5) Dewar, J., *Proc. Roy. Inst. Gt. Brit.* **18**, 435 (1906).
(6) Economos, George, *J. Am. Ceram. Soc.* **38**, 241-4 (1955).
(7) Foote, H.W., Dixon, J.K., *J. Am. Chem. Soc.* **53**, 55-8 (1930).
(8) Gilchrist, E., *Proc. Roy. Soc. Edinburgh* **41**, 128-35 (1920-21).
(9) Hilpert, S., *Chemiker-Ztg.* 34, 1212 (1910).
(10) Hilpert, S., *J. Iron Steel Inst. (London)* **82**, 658 (1910).
(11) Iler, R.K. (to E. I. du Pont de Nemours and Co.), U. S. Patent **2,657,149** (1953).
(12) Ilinski, M., Knorre, G.V., *Ber.* **18**, 699 (1885).
(13) Kearby, K.K. (to Standard Oil Development Co.), U. S. Patent **2,429,319** (1947).
(14) Kelley, G.L., Evers, E.W., *J. Ind. Eng. Chem.* **13**, 1052 (1921).
(15) Krasikov, I.I., Ivanov, I.I., *Trudy Belorus. Sel'skokhoz. Akad.* **8**, 142-4 (1939).
(16) Kwan, T., Fujita, Y., *Bull. Chem. Soc. Japan* **24**, 46-50 (1951).
(17) Kwan, T., Fujita, Y., *J. Research Inst. Catalysis, Hokkaido Univ.* **2**, 110-16 (1953).
(18) Kwan, T., Fujita, Y., *Nature* **171**, 705-6 (1953).
(19) Lanning, C.E., *J. Am. Chem. Soc.* **52**, 2411-5 (1930).
(20) Linde Air Products Co., New York, N. Y. Literature, F-8614, January 1955, form 9691A; F-8601, 8605, December 1954.
(21) Linnell, W.H., *J. Pharm. Soc. Japan* **1**, 178-81 (1928).
(22) McPherson, H.T., Stewart, J., *Biochem. J.* **32**, 763-7 (1938).
(23) MacWhirter, J., *J. Ind. Eng. Chem.* **14**, 462 (1922).
(24) Magnus, A., Roth, H., *Z. anorg. u. allgem. Chem.* **150**, 311-25 (1926).
(25) Makarov, S.Z., Vol'nov, I.I., *Izvest. Akad. Nauk S.S.S.R., Otdel, Khim. Nauk* **1951**, 370-6.
(26) Milner, G.W.C., Woodhead, J.L., *Analyst* **79**, 363 (1954).
(27) Moeller, T., "Inorganic Chemistry-An Advanced Textbook," p. 502, Wiley, New York, 1952.
(28) Neroslavskaya, I.P., Riskin, I.V., Pugacheva, G.I., Russ. Patent **52,904** (March 31, 1938).
(29) Nikitin, N.I., Yuryev, V.I., *Z. anorg. u. allgem. Chem.* **171**, 281-4 (1928).
(30) Nishidoi, T., Setoguchi, M., Japan Patent **416** (1954).
(31) Patrick, W.A., Can. Patent **250,593** (Jan. 9, 1925).
(32) Rowe, H., *Phil. Mag.* [7] **1**, 659-70 (1926).
(33) Sartori, G., *Gazz. chim. ital.* **67**, 98-104 (1937).
(34) Scheermesser, *Chem. Zentr.* [3] **1**, 165 (1870).
(35) See, M.J., Bailie, J.C. (to Standard Oil Development Co.), U. S. Patent **2,455,445** (1948).
(36) Seeliger, R., *Physik. Z.* **22**, 563-8 (1921).
(37) Shapiro, I., Kolthoff, I.M., *J. Am. Chem. Soc.* **72**, 776-82 (1950).
(38) Sheffer, M.L. (to Willson Products, Inc.), U. S. Patent **2,479,520** (Aug. 16, 1949).
(39) Sinkinson, E., Turner, H.G., *Ind. Eng. Chem.* **18**, 602-5 (1926).
(40) Smith, R.A., *Proc. Roy. Soc. (London)* **112A**, 296-303 (1926).
(41) Stetser, J.B., *Chem. & Ind. (London)* **43**, 637-8 (1924).
(42) Taylor, H.S., Burns, R.M., *J. Am. Chem. Soc.* **43**, 1273-89 (1921).
(43) Taylor, H.S., Kistiakowsky, G.B., *Ibid.*, **49**, 2468-76 (1927).
(44) Westvaco Mineral Products Division, Food Machinery and Chemical Corp., New York, N. Y., Tech. Bull., "Sea Sorb Adsorptive Magnesia."
(45) Wildenstein, R., *Mikrochemie ver. Mikrochim. Acta* **39**, 194-5 (1952).
(46) Willard, H.H., Greathouse, L.W., *J. Am. Chem. Soc.* **39**, 2366 (1917).

RECEIVED for review February 13, 1961. Accepted July 20, 1961. Presented in part at the Connecticut Valley Meeting, ACS, November 1960. Investigation supported by contract with Hamilton Standard Division, United Aircraft Corp.

Precombustion Reactions and Knock

G. H. MEGUERIAN and J. F. BUSSERT
Research and Development Department, American Oil Co., Whiting, Ind.

PRECOMBUSTION reactions of hydrocarbons and their knocking tendencies in internal-combustion engines are little understood. Even less is known about the chemical interactions of mixtures of hydrocarbons that lead to the octane number of gasoline. A fundamental knowledge of these reactions could aid in manufacturing more economically the high-octane gasolines.

Ever since the discovery that individual hydrocarbons differ in tendency to knock (*22, 25*), the study of precombustion reactions of hydrocarbons has attracted many investigators. The results of these studies have been adequately reviewed recently (*16, 24*). Many attempts to correlate the engine performance of a wide variety of hydrocarbons with the precombustion properties have met with only partial success. Ignition temperatures, ignition delays, products and total heat of precombustion reactions, positions of cool flames in a tube, and other properties correlate poorly with knocking tendency. A general correlation has not been obtained, probably because either too limited an experimental method was used or knock was not regarded as a composite effect of all precombustion reactions. Only recently has an attempt been made to explain the knocking tendency of hydrocarbons in terms of several characteristics determined under comparable experimental conditions (*27*).

The fuel-air mixture in an engine goes through the entire temperature range of precombustion reactions. Knock occurs when the mixture autoignites before it is engulfed by the flame initiated by the spark (*31*). All types of reactions from initiation of hydrocarbon oxidation through cool-flame reactions to autoignition must take part in producing knock. Furthermore, the importance of these reactions ought to depend on the nature of the hydrocarbons and on the engine conditions.

The importance of various precombustion reactions to the knocking tendency of representative hydrocarbons was studied and areas were defined for further research. The simple, heated-crucible method (*11*) was used, and the reactions were followed by the temperature change in the reacting gas mixture. Several *n*-paraffins, isoparaffins, cycloparaffins, olefins, aromatics, and blends of aromatics in iso-octane were studied. Results were compared with the performance of the hydrocarbons in internal-combustion engines.