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ARTICLES ON THE REMOVAL OF CARBON MONOXIDE WITH SPECIAL REFERENCE TO CARBON MONOXIDE GAS MASKS

BY

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INTRODUCTION

When protection against carbon monoxide and other noxious gases has to be provided by the same gas mask the present practice is to use a combination of filters. All the filters used in industry against carbon monoxide contain manganese peroxide, MnO_2.

It is claimed that the Draeger carbon-monoxide filter offers sufficient protection against carbon monoxide and other noxious gases, and its use is officially recommended for air raid protection in Germany, if necessary after attaching a filter pad to remove solids and liquids (see articles by Bange and Stampe).

The weak point in the industrial carbon monoxide mask is the drying arrangement. A separate and more effective drying attachment would render the carbon monoxide mask more suitable for military purposes.

In the following survey of the literature articles on respirators suitable for use in atmospheres containing carbon monoxide and studies on removal of carbon monoxide from the atmosphere are grouped according to the following headings:

I.   REMOVAL OF CARBON MONOXIDE IN GAS MASK MATERIAL

The following list mentions the most important articles on CO-filters actually used in gas masks for protection against carbon monoxide. It is not to be taken as a critical survey since a portion only of the original articles was available at the time of writing. For this reason the references to Chemical Abstracts (CA) have been added.

1. ALBACH, F. Ten years of gas-mask protection in gas and water
       works. Gasmaske 1:90-92. 1929. C.A. 26:1044. 1932.

   The most important development is the DEGEA CO mask
   (see under WOLLIN).

2. APPAREILS de protection contre les fumées et gaz nocifs.
       Assoc. de documentation scientifique, ind. et commerciale.
       23: 127-135. No. 161. 1933.

   International bibliography, including list of French patents,
   on gas masks and similar apparatus, against harmful gases
   and smoke.

3. BANGERT, Fritz. Mechanism of the carbon monoxide filter.
       Draeger Hefte 194: 3737-3742. 1938.

   The use of the Draeger CO filter depends on the Hopcalite
   (MnO_2 - Cu oxide) catalyst in the gas mask filter. Factors
   which affect the size of the filter, and the reason why a
   CO filter cannot be used against concentrations of CO
   greater than 2% are discussed. A sectional view of the
   Draeger CO filter is shown. It has not been possible to
   obtain a catalyzer for CO combustion insensitive to mois-
   ture. The drying medium accounts for the bulk of the CO
   filter since the normal moisture content of air at 20°C.
   exceeds 20 g. per cu. m. A second drying mass is placed
   on the opposite face, near the mouth of the wearer to pre-
   vent respiration moisture from leaking into the CO filter.
   In extremely dry air the filter would last for many hundred
   hours.

   Poison gases as well as water vapour reduce the activity of
   the filter if allowed to remain in contact with the catalyzer.
   Many poisons are not only adsorbed but chemically altered
   and retained (HCN, H_2S) by the active mass. A carbon mon-
   oxide filter protects the wearer against any type of poison
   gas, but this property is not useful in industry, because
   there are cheaper means of protection against poison gases
   other than carbon monoxide. The presence of poisonous
   vapours reduces the degree of protection against carbon
   monoxide, and the filter must be changed after 20 hours for
   reasons of safety unless a means is provided for removing
   poison gases or vapours other than CO before they enter the
   CO mask. The thread connection of the inhalation valve of
   the Draeger filter allows the attachment of any normal
   industrial filter. Such a combination is used, in particular,
   in air raid protection, where a filter against suspension is
   added (blue cross).

The Draeger CO filter is safe to use for the number of hours indicated on the filter (20 hours) providing that the CO content remains below 2%. Since the reaction $2CO + O_2 = 2CO_2 + 67$ kg.cal. takes place in the filter, a 2% concentration of CO in the inhaled air means a 2% concentration of CO_2 in the filtered air that is breathed in. With 30 l. of air per minute the filter would produce $30 \times 20 \times 60 \times 0.02 = 720$ l. CO_2 during its normal life of 20 hours. It is not possible to absorb this gas volume without unduly adding to the weight of the filter, and this consideration restricts th use of the filter to CO concentrations below 2%. Another reason is the amount of heat produced by the reaction, an increase of 60°C. for 30 l. per minute with 1% CO, and 100°C. for 2% CO.

The Draeger CO filter consists of outer thread connection, inhalation valve, cotton wool, drying mass, catalyst, drying mass, resistance warner (in which moisture increases the resistance to flow), cotton wool, screwed plug. It is attached to a gas mask or to a rubber connection.

Stored unused carbon monoxide filters are good for four years, when used once for four months (page 3763).

4. BANGERT, Fritz. Remarks on the chemistry of the people's gas mask. Angewandte Chemie 51:209-212. 1938.

In his "remarks on the chemistry of the people's gas mask" Fritz Bangert of the Division of Chemistry, Draeger Works, Lubeck, reports that neither the air defence gas mask S, nor the civilian gas mask, VM37, protects against carbon monoxide. He adds that carbon monoxide is not a chemical weapon and will not be used as weapon in future wars. It will appear only where it is found normally in peace time, near broken gas pipes, gas reservoirs. The points where carbon monoxide may escape during air attacks have to be taken into consideration when the S mask is used or when the latest type of civilian gas mask is used, or when the protection of factories is to be ensured. Pipes that cross air raid shelters, or that pass near air raid shelters, must be equipped with valves. The wearer of the civilian gas mask is in general free to avoid other possible sources of carbon monoxide.

The active material in the S mask consists of a uniform layer filling the whole filter, and consisting of a fibrous material in which are embedded uniform grains of active charcoal. The grains have diameters between 1 and 3 millimetres.

5. BRUNS, B. Reaction mechanism of the oxidation of carbon
   monoxide on the hopcalite surface.
   II. Function of hopcalite-bound water in the catalytic
   process. Acta Physicochimica U.R.S.S. 7:875-882. 1937.

   Hopcalite mixture prepared according to W.A. Whitesell and
   J.C.W. Frazer, with 70% MnO_2 and 30% CuO (J. Am. Chem. Soc.
   45: 2841-2851. 1923) contains considerable bound water
   which is removed by degassing at 180^oC.(giving about 40 cc.
   H_2O vapour from 1 g. Hopcalite).

   Undehydrated hopcalite readily becomes reduced during the
   $2CO + O_2 = 2 CO_2$ surface reaction and loses activity, while the
   thoroughly dehydrated catalyst retains its full high and
   uniform activity for a long time. because in its presence
   the oxidation of CO (8.4 mm. Hg) to CO_2 consumes exclusively
   the oxygen (8.4 mm. Hg) in the surrounding atmosphere.
   Reduction of the catalyzer itself by CO takes place in the
   absence of O_2.

   The catalyzer adsorbs water but gives it off at 25^oC. and
   recovers its former activity.

   (For part I see SHURMOWSKAJA and BRUNS)

6. BURRELL, Guy H. Development of gas mask by Bureau of Mines,
   absorbs carbon monoxide from inspired air. Coal Age. 20:
   635-636. 1921.

   Research resulted in production of Hopcalite, a mixture
   of oxides of manganese and copper which absorbs carbon
   monoxide.

7. CHARACHORIN, F., S. ELOWITZ and S. ROGINSKY. The mechanism
   of the catalytic oxidation of carbon monoxide on manganese
   dioxide. III. Existence of a critical low pressure limit
   in heterogeneous oxidation. Acta Physicochim. U.R.S.S.
   3: 503-508. 1935. C.A. 30:7987. 1936.

   At pressures from 1 atm. down to 10 mm. the oxidation of
   CO by O_2 on a MnO_2 surface is approximately a first order
   reaction independent of the oxygen pressure, the heat of
   activation being equal to 6000 cal.

   At pressures below 0.525 mm. the reaction is almost of
   zero order and is practically independent of the temperature.
   The molecular oxygen present in the air is not used up
   whereas at higher pressures the CO is oxidized by oxygen
   in the gaseous phase. Oxidation at low pressures is rapid,
   even at -78^oC.

the high pressure reaction follows immediately the process of activated adsorption of a molecule of CO on MnO_2, the low temperature reaction is not related to activated adsorption, since adsorption at low pressures is still quite rapid down to -78^OC., the temperature at which activated adsorption is too slow to be measured. Activated adsorption is not a necessary condition for catalytic action. Activated adsorption of CO and the kinetics of the catalytic reaction have almost the same rate and the same temperature coefficient at high pressures and temperatures higher than -20^OC., but differ greatly at lower pressures and temperatures.

(For part II see ROGINSKY)

8. CHARACHORIN, F. and S. ELOVITZ. Mechanism of the oxidation of carbon monoxide on manganese dioxide. IV. Adsorption of carbon monoxide and dioxide at low pressures (between 10^{-3} mm. and 3 mm. Hg). Acta Physicochim. U.R.S.S. 5:325-354. 1936. C.A. 31: 6078. 1937.

Studies under way since 1932 suggest that CO is adsorbed in an activated state on MnO_2. In an atmosphere of CO it reacts with the oxygen of MnO_2 and produces CO_2 and MnO. In an atmosphere containing oxygen in addition to CO, it reacts with oxygen molecules impinging upon the surface provided that the impacts follow the adsorption before the reaction with the solid has had time to take place.

Adsorption of normal molecules of CO on MnO_2 (0.1 g.) predominates at low temperatures, adsorption of activated molecules above -78.5^OC. Both types are present between 200 and 300^OK. At 300^OK. the molecular adsorption is negligible. The energy of activation is variable but measures at least 6,225 cal. About 5×10^{20} active adsorption points are found for 1 g. MnO_2, this is equivalent to 10% of the surface. At 50^OC. a mass of 0.1 g. of freshly prepared MnO_2 adsorbs 2×10^{18} molecules in one minute, and changes them to CO_2 with a temperature increase of 0.1^OC.; a mass on which adsorption has previously taken place adsorbs 10×10^{17} molecules at 17.4^OC. The most active points are the first to be occupied and require small activation energies. Heat of molecular adsorption of CO is 2300 cal.

Activated adsorption of CO_2 is observed at temperatures higher than 25^OC.

9. CHEMISCH-TECHNISCHE REICHSANSTALT. Alarm devices for indicating the presence of dangerous gases and vapors. Z.ges. Schiess Sprengstoffw. 34:337-339. 1939.

> Upper and lower explosive limits for 18 combustible gases and conc. for 16 poisonous gases.

10. DAVIS, F. Rutledge (Davis Emergency Equipment Co. N.Y.) Respirators for chemical safety. Chemical and Met. Engineering. 46: 143-145. 1939.

> Carbon monoxide does not fit into any of the groups of noxious gases and vapours, being neither a simple asphyxiant, nor an acid or alkaline gas, or organic vapour. It requires special consideration.

> A very few types of chemical filters will handle the great majority of noxious gases encountered in industry, these filters are supplied in canisters that are standardized as to colour and range in capacity from 300 cc. to 2,000 cc. (for acid gases, white, HCN white with green stripe, ammonia green, organic vapours black, carbon monoxide blue, organic vapours and acid gases yellow, organic vapours, acid gases and ammonia brown, "All Service" (all gases mentioned) red).

> The chemicals used are soda-lime for acid gases; copper sulphate, or silica jel or organic acids for ammonia, activated carbon for organic vapours, hopcalite for carbon monoxide.

> The combination canisters (yellow, brown, or red) contain two or more kinds of filters.

> Any of these canisters can be supplied with filter pads to provide protection against smoke and dust.

11. DESGREZ, A., H.GUILLEMARD, A.HEMMERDINGER and A. LABAT. Fixation of carbon monoxide diluted and carried in a stream of air. Chimie et industrie 6:118-123. 1921. Académie des Sc. 173: 186-188. 1921.

> The known reactions are not satisfactory for use in gas mask filters. The rate of reaction of I_2O_5, although not sufficient even at $50^{\circ}C$. is accelerated by the addition of one-third of its weight of H_2SO_4 deposited on pumice, (round grains about 4 mm. in diameter). A mass of 85 g. of granulated pumice, 18 cc. H_2SO_4 of 66 B., and 70 g. I_2O5 traversed by a stream of 7 l.of air per minute, with 0.8% CO, oxidizes all the CO when the temperature exceeds 35°.

12. ELKINS, Hervey B. Toxic fumes. Ind. Med. 8: 426-432. 1939.
    C.A. 34:5198. 1940.

The toxic concentrations were determined in a number of
Massachusetts industries. Up to 300 determinations were
made. In 1937, 47% of the tests showed unsafe concentra-
tion; in 1938, only 31%. Maximum allowable concentrations
were in mg. per 1,000 litres.

	mg./1000 litres
CCl_4, ethylene dichloride, NH_4OH, CO	100
Benzene, dichlorobenzene	75
HCN, HCHO, H_2S	20
CS_2	15
HCl, NO_2, SO_2	10
Aniline, nitrobenzene	5
HF	3

(The unbearable concentrations of war-gases vary from 0.1 mg.
per litre for chlorine to 0.001 (or 1 mg. per 1000 litres)
for mustard gas (dichlorodiethyl-sulphide) and 0.0007 mg.
per l. for camite (brom-benzyl-cyanide)).

13. ELOVITZ, S. and S. ROGINSKY. Mechanism of the oxidation of
    carbon monoxide on manganese oxide. V. Kinetics of the
    carbon monoxide oxidation on manganese oxide at pressures
    over 30 mm. (30 to 500 mm. Hg). Acta Physicochimica
    URSS. 7: 295-310. 1937. C.A. 32: 3243. 1938.

The oxidation of CO on MnO_2 in the presence of oxygen was
studied at 17°, 0°, -21.2° and -38.8° and pressures of 30 mm.
to 500 mm. Hg. The activation energy is 6,300 cal.

The mechanism in this range is that of an activated adsorp-
tion of CO on MnO_2, the rate equation being
$$dq/dt = a \exp. (-bq),$$
where q is the amount of CO previously adsorbed on MnO_2.

For part IV see CHARACHORIN.

14. ELOVICH, S. YU. and V.A. KORNDORF. Mechanism of catalytic
    oxidation on manganese oxide VI. Influence of water vapor
    on the reaction kinetics. VII. Reaction kinetics. J. Gen.
    Chem. U.S.S.R. 9: 673-681, 714-728. 1939. C.A. 33:9101. 1939.

The reaction velocity is almost independent of O_2 conc. and
proportional to the CO concn.

The exptl. data are in accordance with the formula dq/dt a exp. $(-a_1 q)$ when the amount of chemisorption is 2% or more; when it is small, about 1%, a first order reaction takes place.

The presence of CO_2 has little influence upon velocity and results.

When MnO_2 is dried at $180^{\circ}C$. the unhomogeneous character of the mass is increased.

15. FIELDNER, ..C., K.TZ, S.H. and REYNOLDS, D.... The carbon monoxide self-rescuer. U.S. Bureau of Mines, Reports of Investigations, No. 2591. 10 p. 1924.

16. FIELDNER, ..C., K.TZ, S.H., FREVERT and MEITER. All-Service gas mask for protection in air against all gases, vapors and smokes. U.S. Bureau of Mines. Reports of Investigations. 2719. 1925.

17. FR..ZER, J.C.W. Catalytic oxidation of carbon monoxide. J. Phys. Chem. 35: 405-411. 1931.

The first catalyst, developed with Roger, Piggot, Bahlke and Jennings (J. Am. Chem. Soc. 43: 1973. 1921), consisted of MnO_2 and silver oxide. Shortly afterwards Whitesell and Frazer prepared a catalyst equally good from MnO_2 and copper oxide. MnO_2 alone is equally good if the possibility of contamination with adsorbed material is eliminated in its preparation. Williams (Dissertation Johns Hopkins U. 1928) prepared finely divided cobaltic oxide and Bennett (Dissertation 1930) nickelic oxide as catalysts.

Seventeen other oxides were prepared in finely divided condition but only one of them, ferric oxide, showed some activity below $100^{\circ}C$.

Manganese oxide, cobaltic oxide and nickelic oxide show a variable oxygen content, being mixtures of more than one oxide, and give up or take up oxygen continuously according to conditions.

18. G..RNER, W.E. and W..RD, T. The heats of adsorption of gases on the oxides of manganese at low pressures and room temperatures. J. Chem. Soc. 1939: 857-864.

Adsorption of CO on the oxidized surface is followed by a slow evolution of heat.

19. GEHRMANN, Fritz. Carbon monoxide. Gasmaske 11: 97-101. 1939.
       C.A. 34: 1093. 1940.

    Primarily a historical treatment of the toxic effects of
    CO, brief directions for treatment and description of Auer
    CO detector.

    The detector is based on the reaction of CO with a mixture
    of I_2O_5 and fuming H_2SO_4, liberating I, which colors the
    liquid.

20. GRAHAM, J.I. Respirators for absorbing carbon monoxide.
       Colliery Guardian 128: 1635-1636. 1924.

    Tests are described to determine the efficiency of the
    Burrell All-Service canister (No. CO-10) and the M.S.A.
    self-rescuer.

21. HANSLIAN, Dr. Rud. Der chemische Krieg. E.S. Mittler und
       Sohn. Berlin. 1937.

    (P. 425) Protection against carbon monoxide is of interest
    in peace time to industrial concerns and fire fighters; but
    carbon monoxide plays also an important secondary part in
    air raid attacks.

    CO occupies a unique position among the noxious gases; no
    filters were available for a long time for this gas; on
    account of its low boiling point and the chemical inertness
    of the gas at room temperature adsorption and chemical
    fixation are very difficult. It is necessary to burn it to
    CO_2. Combustion of CO with the aid of I_2O_5 in the D.Z.
    (special Desprez filter with I_2O_5 on pumice grains, dipped
    in concentrated H_2SO_4, and Na_2O), a filter that protected
    for 75 minutes against a concentration of 1/1000 was
    abandoned in the post-war period.

    Investigators in the United States have used a mixture of
    metallic oxides that is capable of oxidizing carbon monoxide
    and organic compounds, including hydrocarbons. The mixture,
    called Hopcalite, consisted in the beginning of manganese
    peroxide, and the oxides of copper, cobalt and silver in
    the approximate ratio 50:30:15:5, but is now made of the
    two components manganese peroxide (about 60%) and copper
    oxide (about 40%).

    The catalyzer must be kept dry.

    The normal carbon monoxide filter is about 25 cm. high and
    weighs 2.5 to 3 kg.; its useful life is less than 40 hours,
    25 hours on the average.

Since the catalyzer gives a considerable degree of protection against all known gases and vapours although its catalytic properties occupy first place, it is not absolutely necessary to combine it with filters against other noxious vapours. An increased degree of protection is obtained with the Universal CO filter in which baffles and active charcoal, and a second pair of catalyzer and drying layers have been added.

22. HEINRICH, F. and PETZOLD. Testing a carbon monoxide gas-mask. Chem. Fabrik 19-22. 1928. C.A. 22: 3005. 1928.

The DEGEA gas-mask for use in atmospheres containing CO consists of a filter impregnated with a catalyst, which promotes the oxidation of the CO to CO_2 by the O in the air, and is provided with an indicator which liberates C_2H_2 as a warning when the efficiency of the filter begins to be impaired. In air containing 1.5% CO the life of the filter is about 40 minutes, and in air containing 4.4% CO about 10 minutes.

To test the efficiency of the mask the gases are passed through at a definite velocity, thence through K mercuric iodide to remove C_2H_2, conc. H_2SO_4 to absorb hydrocarbons, $CaCl_2$ and P_2O_5 to remove moisture, and soda-lime and P_2O_5 to absorb CO_2, and finally over CuO at 300°, any CO_2 formed being absorbed in soda-lime after drying in the usual way. For qual. detection of minute traces of CO the blood test gives the most dependable results; the ammoniacal silver solution and palladous chloride tests are uncertain in the presence of H, C_2H_2 and CO_2.

The tests were made at the research laboratory of the HOESCH steel plant in DORTMUND.

23. HOFF, C.v. Tests of carbon monoxide filter of DEGEA design. Glückauf 64: 1415-1418. 1928.

24. JORG, Heinrich. War gases, gas-protective devices and their applications in time of peace. Oesterr. Chem. Ztg. 30: 35-38, 46-49. 1927. C.A. 21: 1858. 1927.

The inefficiency of carbon (from heating conifers impregnated with $ZnCl_2$, charcoal from coconuts and other tropical nuts, cherry pits, peach stones, apricot pits) against CO and dusts is pointed out.

For oxidation of CO the use of I_2O_5 in fuming H_2SO_4 is recommended, but hopcalite (MnO_2 with CuO, Ag_2O and cobalt oxides), preceded by $CaCl_2$, is preferred.

25. KATZ, S.H., J.J. BLOOMFIELD and A.C. FIELDNER. The Universal and the Fireman's Gas Masks. U.S. Bureau of Mines Tech. Paper 300. 1923.

Description, tests, limitations, standard test requirements, chemical stability. Publications on gas masks and breathing apparatus.

26. KATZ, S.H., McCAA, G.S. and BARTH, A.L. Use of carbon monoxide gas masks in mines. Carnegie Inst. of Tech. Coal Mining Investigations. Bull. 14. 72 pp. 1924.

The All-Service masks may be safely used as long as a flame can be maintained in a safety lamp. The safety lamp requires 16% O_2, whereas man is not endangered until the O_2 content is reduced to 12 or 13%.

27. KATZ, S.H. Industrial gas masks abroad. U.S. Bureau of Mines. Inf. Circular 6206. 1929.

Industrial gas masks, manufacturing plants, organizations, and laboratories dealing therewith, carbon monoxide gas masks proposed for use in mines.

28. KATZ, S.H. and GRICE, C.S.W. Mine rescue apparatus: the S.M.R.B. gas mask. Safety Mines Research Board (London). Papers No. 57: 3-37. 1930. C.A. 24: 1910. 1930.

Results of chemical tests at Sheffield on the S.M.R.B. canister are tabulated for acid gases, CCl_4, NH_3, and CO, and show satisfactory results.

The canister contains: cotton wool, $CaCl_2$, hopcalite, silica gel, $CaCl_2$, caustic pumice, cotton wool and activated charcoal in thin layers, in total amounts similar to those of Bureau of Mines canister.

29. KHODOT, V. Permeability of rubber in respirators at higher temperatures. Caoutchouc and Rubber. U.S.S.R. 1937. No. 1: 21-30.

30. LAMB, Arthur B., BRAY, Wm. C. and FRAZER, J.C.W. Removal of carbon monoxide from the air. J. Ind. Eng. Chem. 12: 213-221. 1920. C.A. 18: 1009. 1920.

One molecule of the expensive O_3 under favorable conditions will oxidize one mol. of CO

I_2O_5 with fuming H_2SO_4 works well and a little free I present at the start improves the "pick up". The excess heat may be taken care of by allowing it to melt $Na_2S_2O_3 \cdot 5H_2O$.

Pd has a catalytic action but is too sensitive to impurities.

The costly $AgMnO_4$ acts slowly, with $CaCl_2$ too violently, but the further addition of CaO would control the reaction.

Mixtures of oxides were tried out as oxidizers or catalyzers. The mixtures $CuO + Ag_2O$, $CuO + Co_2O_3$, $MnO_2 + Ag_2O$ all gave promise.

Finally hopcalite was evolved, consisting of a catal. mixture of 50% MnO_2, 30% CuO, 15% Co_2O_3, 5% Ag_2O.

Drying of the air by a special $CaCl_2$ was necessary, since H_2O slows up the reaction.

A table is given for the length of service under different conditions of the navy canister containing this material.

31. MIELENZ, W. Possibility of using carbon monoxide as a war gas. Gasschutz Luftschutz 5: 263-267. 1937. C... 30: 185. 1936.

Mielenz disagrees with Hanne (Marcel Hanne, Industrie chimique 22: 322-326. 1935) in the latter's conclusion that CO will occupy a prominent place as a war gas in future wars.

32. MIX, K. Prevention and cure of carbon monoxide poisoning. Gesundheits Ing. 56: 292-294. 1933.

The necessity of adding drying materials makes the filters rather voluminous and has led to the construction of larger types of respirators in which the filter is placed under the arm and connected with a tube to mouthpiece or mask (Draeger and Degea). These respirators are intended for work in hazardous places.

The respirators in which the filter is part of the gas mask are intended for emergencies (Degea 1 hour, Draeger $\frac{1}{2}$ hour).

The use of all filters against CO depends on the concemtration of oxygen and carbon monoxide (oxygen not much below 17%, carbon monoxide not more than 2%). Beyond this limit it is necessary to use oxygen.

33. MUSCHENBORN, H. Carbon monoxide filters under various
      laboratory conditions. DRAEGER HEFTE 198:3959-61.
      1938. C.A. 33:1177. 1939.

CO filters were tested under relative humidities of 25%,
50%, 75% and 90% with CO conc. of 0.1, 1.0 and 2.0
vol.% and with air volumes through the filter of 20,
40 and 60 l. per minute, in each case for ½ hour.
Results are given in terms of hours before CO pene-
trates the filter and causes the concentration to in-
crease to 0.03%. In general this time decreased with
increase of relative humidity, by 20% when the humidity
increased from 25 to 90% relative humidity at 20 l.
air per minute, 30% at 40 l. air per minute, and
about 35% at 60 l. air per minute.

The concentration of CO from 0.1 to 2.0 vol.% made
little difference in the temperature produced in the
filters.

20 l. air per minute

Rel. hum. %	CO conc. %	Break hours	CO transformed litres	Increase in temp. °C
	0.1	31.5	19.1	14.8
25%	1.0	30.6	183.5	36.9
	2.0	29.1	349.6	44.2
	0.1	30.4	18.2	16.1
50%	1.0	29.7	178.1	39.2
	2.0	28.2	338.2	46.8
	0.1	28.0	16.8	17.2
75%	1.0	27.2	164.0	41.8
	2.0	26.3	316.2	50.3

The resistance to flow increased from 12
or 15 mm. water column to 40 or 45 mm.
water column.

60 litres air per minute

	0.1	15.2	27.6	22.2
25%	1.0	14.1	255.1	42.8
	2.0	12.8	463.2	69.0
	0.1	13.1	23.6	24.0
50%	1.0	11.8	213.6	45.1
	2.0	11.0	396.1	74.6
	0.1	11.4	20.5	24.9
75%	1.0	10.2	186.6	47.3
	2.0	9.1	327.6	79.0
	0.1	9.8	17.6	25.2
90%	1.0	9.0	162.0	50.3
	2.0	8.3	298.8	88.0

34. PICK, H.   Catalytic filters, carbon monoxide filters.

ULLMANN, F. Enzyklopädie
tech. Chemie 9 (197/198) 1932

The reaction

$$2CO + O_2 \rightarrow 2CO_2$$

between carbon monoxide and the oxygen in the atmosphere
does not take place at ordinary temperature unless certain
catalyzers such as have been discovered by investigators
in the United States are present. They bring about com-
plete combustion at room temperature as well as at tem-
peratures obtaining in winter. (Draper Journ. Amer. chem.
Soc. 50: 2637. 1928, Pieters, Chem. Weekblad 28:250
1931. B. Neumann, Kroger and Iwanowski, Zeitschr. Elek-
trochemie 37:121. 1931, with older literature.)

The mixtures of oxides used for this purpose contain
manganese peroxide (MnO_2) and oxides of cobalt, copper
and silver, precipitated and granulated according to a
certain method. The mass is called Hopcalite (U.S. Patent
1,345,323. W.A. WHITESELL and J.C.W. FRAZER J.Am. Chem.
Soc. 45:2841-51. 1923). The first mask equipped with
Hopcalite seems to have been theM.S.A. self-rescuer of
the Mine Safety Appliances Co. Pittsburgh, Pa. (1924).
It was intended exclusively for protection against
carbon monoxide. The same firm produced in addition the
All-Service mask for industrial uses and for fire-fighting.
(Ind. Eng. Chem. 22:1096. 1930). These masks are the
only/respirators approved by the U.S. Bureau of Mines for
protection against carbon monoxide (Inform. Circ. 6918,
Oct. 1936). The canister contains the following layers,
listed in the order from bottom to top:

Activated wood charcoal, impregnated with $CuSO_4$	400 cc
Activated wood charcoal	200 cc
Caustic soda preparation	200 cc
Cotton filter	
Calcium chloride, free from water	200 cc
Hopcalite	300 cc
Calcium chloride, free from water	100 cc
Cotton filter	

The catalytic action of Hopcalite is destroyed by water
and water vapour. This explains the insertion of calcium
chloride layers. As soon as the drying action is ex-
hausted the carbon monoxide penetrates.

The carbon monoxide mask of the DEGEA (Deutsche Auer Gesellschaft) embodies means for warning the bearer through the odor of acetylene when the drying layers are exhausted (German Pat. 444,486, 1926). DRAEGER uses the increase in resistance to breathing for this purpose. Since the catalytic oxidation of carbon monoxide is based on the oxygen content of the atmosphere, the application of the carbon monoxide canister is restricted to oxygen concentrations of at least 6%.

35. PATENTS:

(a) AUER GESELLSCHAFT A.G. (Heinz Eisenbarth)

Respirator Ger. P. 671, 176 Feb. 11, 1939 (bl.6/a.29.30)
(CA. 33:3486. 1939)
A respirator filter for protection against CO comprises a number of oxidation catalyst layers of successively increasing activity, thelayer of lowest activity being nearest to the air inlet.

(b) DAVIS, Sir R.H. and Levy, L.A.

Respiratory applicances; drying agents

Brit. Pat. 499, 038 July 19, 1937

For a respirator for use in atmospheres containing carbon monoxide, wherein the latter is removed from the inspired air by catalytic oxidation, after passage through a drying medium, the drying medium comprises two layers of material disposed in succession in the path of the air, and composed, the first of fused zinc chloride dispersed on a carrier, preferably active charcoal, and the second of a granulated mixture of calcium chloride and fused zinc chloride. A third layer of magnesium perchlorate granules may be provided.

The material of the first layer may be made, for example, by mixing 9 parts of dry charcoal granules with 15 parts of fused zinc chloride, and stirring the mixture until cool enough for the granules to remain non-adherent to one another, and that of the second layer by mixing powdered anhydrous calcium chloride with about 20 per cent of fused zinc chloride, and when cold, granulating the mixture.

Reference is made to the use of the known oxidizing catalyst for carbon monoxide consisting of a mixture of manganese and copper oxides to which a small quantity of another oxide, such as of silver, is added.

35. PATENTS:

(c) Drägerwerk HEINRICH and Bernhard DRAGER

Gas masks

German Pat. 631,346 June 17, 1936
Cl.61a 29.30

Ca 30: 6088. 1936

A mask for protection against CO may comprise a layer of the oxidation catalyst sold under the name "hopcalite" and a layer of CaC_2.

The air first comes into contact with CaC_2, whereby water vapour which poisons hopcalite, is converted into C_2H_2. CO and C_2H_2 are converted by the hopcalite into CO_2 and H_2O until the hopcalite is exhausted whereupon the smell of C_2H_2 warns the wearer.

Layers of a drying agent, e.g. $CaCl_2$, may be arranged in advance of the CaC_2 layer and behind the catalyst layer.

(d) FINN, John

Catalytic device suitable for treating engine exhaust gases.

U.S. Pat. 2,106,910, Febr. 1, 1938
Ca 32: 2719. 1938

A catalytic material such as NiCuCo nitrate is dispersed in a frangible matrix contg. finely divided particles of unannealed fused siliceous material (glass) and a binder such as lime or plaster of Paris.

(e) FRAZER, Joseph C.W.,

Catalyst for oxidation of carbon monoxide

Can. Pat. 368,866 Sept. 21,1937.
U.S. Pat. 2,092, 059 Sept, 7, 1937

A Cu chromite catalyst is prepared by dissolving a soluble compound of Cu in chromic acid sol. in amounts to form Cu chromate, and heating the product.

35. PATENTS:

(f) LOMBARD-GERIN, LEON

Carbon monoxide

Brit. Pat. 482,654 Mar. 30, 1938

CO is continuously absorbed from industrial gases by means
of a sol. obtained by dissolving cuprous chloride (Cu_2Cl_2)
in a solv. of two or more of the chlorides of K, Na, NH_4,
Mg, Ca, Al, Fe, Mn, Ni and Cu (cupric). The CO may be
recovered from the solv. by the application of a vacuum. A
preferred solution is a saturated aqueous solution of KCl,
NaCl and NH_4Cl in which sufficient cuprous chloride is
dissolved to make the concentration in monovalent copper
30%.

An apparatus for conducting the process comprises an ab-
sorption column filled with Raschig rings and a recovery
column to which a vacuum is applied.

(g) OLIVIERO, Mathurin-Joseph

Filter for gas mask.

Fr. Pat. 45301, addition to 777, 991 22 July, 1935

The filter comprises a layer of cloth impregnated with
sulfonal and succin, a layer of cloth impregnated with an
alkali cinnamate, a catalyst composed of Cr_2O_3 to oxidize
CO to CO_2 which is absorbed by soda lime, pumice impreg-
nated with oxides and reduced metals such as Ni, Cu, Mn,
Sn and Ag, and finally a layer of activated charcoal.

(h) "SICAA"

(Société an. société industrielle constructions
antiaériennes Antigaz)

Swiss Pat. 198,754, Nov. 16, 1938   (Cl.57)

(i) I.G. FARBENIND. A.G. (Wilhelm Wenzel)

Catalyst for oxidation processes.

Ger. Pat. 649,589 Sept. 1, 1937 (Cl.12e 3.01)

The catalyst consists of manganite of metals other than Mn,
the oxides of which have no basic properties.

35. PATENTS:

(j) A new cartridge for absorbing carbon monoxide

Colliery Guardian 138:730. 1929
(Eng. Index p.852. 1929)

Note on DEGEA device for filtering carbon monoxide gas
in respirators and similar breathing apparatus. Type
illustrated can be used with safety where air breathed
contains up to 6% carbon monoxide, and for periods up to
15 hours. (Another brief description in Iron and Coal
Trades Rev. 118:43 1929).

36. POLACZEK, P.

Respiratory poisons and filtering equipment

V.D.I. Zeits. 75:1411-1414. 1931

Filtering equipment with particular regard to types suit-
able for protection in industry against all kinds of gas,
dust, etc.

37. ROGINSKY, S.

Mechanism of catalytic oxidation by molecular oxygen at
low temperatures.

Acta Physico chim. U.R.S.S. 9:475-500 1938

NO on SiO_2, CO on MnO_2, H_2 on Pt and Pd are discussed.
Hydrogen is readily oxidized in contact with Pt, Pd and
oxygen; CO poisons these catalysts. In the presence of
MnO_2 on the contrary, CO is oxidized to the exclusion of
H_2, even when the concentration of CO is only 1/100 or
1/1000 of that of H_2. Water vapour poisons MnO_2, but
not Pt and Pd.

The following mechanism is proposed:
1. $MnO_2 + CO = MnO_2(CO)$ activated adsorption
2. $MnO_2(CO) = MnO_2 + (CO)$ desorption
3. $MnO_2(CO)+O_2=MnO_2(O)+CO_2$ oxidation (first step)
4. $MnO_2(O)+CO = MnO_2+CO_2$ "   (second step)
5. $MnO_2(CO) = MnO_2 + CO_2$ chemisorption
6. $MnO+\frac{1}{2}O_2 = MnO_2$ regeneration of CO.

38. ROGINSKI, S. and J. ZELDOWITCH

The catalytic oxidation of carbon monoxide on manganese dioxide.

ACTA PHYSICO CHIMICA U.R.S.S. 1:554-594. 1934
CA 29: 7776. 1935

The heats of adsorption of normal molecules on MnO_2 are 2300 cal. per mol. for O_2, 2,600 for CO, 3400 for N_2, 5,500 for CO_2, and 12,000 for H_2O and C_6H . The isotherms of molecular adsorption follow Freundlich's rule for low pressure (below 100 mm) and Langmuir's rule for high pressure and coverage, which is an unexpected result. An extrapolation on Langmuir's isotherm shows that at saturation 1 g. of powder takes up 18 cc. CO near room temperature, corresponding to a monomolecular layer.

The heats of activation of O_2 and CO on the catalyst are 11,000 for O_2 and 7,000 cal per mol. for CO.

The sample of MnO_2 (0.1g.) had a surface of about 1 sq. metre and was practically free from other metals; it was dried for three hours in a thermostat at $180^{\circ}C$. The carbon monoxide is not immediately oxidized because the oxidation is not reversible under the condition of the experiments. The first cc are rapidly adsorbed, within the first few minutes; the rate decreases afterwards owing to the increase in temperature produced by the heat of adsorption, about 6,000 cal. per mol. (oxidation and adsorption of CO_2).

With activated adsorption the temperature increase may exceed $20^{\circ}C$ at $0^{\circ}C$. The time necessary for adsorption of 1 cc(N.P.T.) at $-39^{\circ}C$ and 760 mm is given by the relation

$$\ln T = 0.069 + 0.465 \ q$$

where q is the number of cc already adsorbed.

39. ROGINSKY, S. and J. ZELDOWITSCH

The catalytic oxidation of CO on MnO_2
(I and II)

ACTA PHYSICO CHIMICA
(Part I) 1:554-594, 1934
(" II) 1:595-610, 1934
CA 29: 7776. 1935

Part I is a systematic investigation of the adsorption of CO, O_2 and CO_2 on catalytic MnO_2. The results obtained in Part II indicate that there is no time lag between the activated adsorption of CO and the reaction $CO + MnO_2 \rightarrow CO_2 + MnO$

The speed of CO adsorption with constant amounts of CO_2 at the surface is proportional to the amount of accessible O_2 in the MnO_2 surface.

The speed of O_2 regeneration by oxidation of the reduced $MnO2$ is much slower than the speed with which $O2$ is used in the catalysis.

The measurements are not in agreement with the theory that catalytic oxidation involves three stages: (1) activated adsorption with chemical reaction,(2) appearance of carbon dioxide in the gas phase,(3) regeneration of reduced point on the MnO_2 surface with the aid of oxygen in the gas phase.

40. RUMPF, H.

The "DEGEA" (carbon monoxide) gas mask.

Gas und Wasserfach 70:268-270. 1927

The use of the mask is described, but its construction and filling are not discussed.

41. SENATOROFF, N.K.

(Mine Safety Appliance Co.'s) Carbon monoxide indicator for analysis of combustion products of natural gas.

Pac. Coast Gas Assn. Proc. 26:46-47. 1935

42. SHURMOVSKAYA, N. and B. BRUNS

Mechanism of the catalysis of the oxidation of carbon monoxide on a hopcalite surface
I Poisoning of hopcalite by water vapour.

Acta Physicochim U.R.S.S. 6:513-530. 1937.
J. Phys. Chem. U.S.S.R. 9:301-312. 1937.
CA 31:6542. 1937

Adsorption data for H_2O on hopcalite at 30 to 50° and 0.26 to 11 mm. satisfy $A = RT \ln p_s/p$.

Oxidation of CO in 0.5% CO-air mixtures proceeds in 2 steps: (1) oxidation by O from MnO_2, followed by (2) oxidation by molecular O_2.

On a hopcalite catalyst containing 70% MnO_2 and 30% CuO, the reaction is of zero order.

The energy of activation varies from 5,000 to 7,000 cal.

As the quantity of adsorbed moisture increases, the velocity of oxidation falls linearly and becomes 0 at 2.7% H_2O. The hopcalite surface consists of two regions having resp. the heats of wetting 7,200 cal. and 500 cal. per mole H_2O.

43. SMOLCZYK, Ed. The second decade in gas protection. Gasmaske 11:110-130. 1939.

History of the development of all types of gas protection, illustrated by many photographs.

44. SPAUSTA, F. Detection and determination of small amounts of carbon monoxide in air. Chem. App. 25:137-141. 155-160. 177-181. 1938.

Review and bibliography.

45. STAMPE, Gerhard and SOMMER, Otto. The Draeger carbon monoxide filter lll. Draeger Hefte No. 180. 2987-2989. 1935.

Improvements in the CO gas mask filter are described.

46. STAMPE, G. Draeger carbon monoxide filter apparatus with mechanical chronometer. Draeger Gas schutz Mitt. 1929 No 10: 37-39 C.A. 24:5538. 1930.

The apparatus consists of a suction device whereby the CO passes through a removable cartridge where it is oxidized to CO_2 and the amount read directly on a scale.

The cartridges last for about 4 hrs. after which they have to be replaced. CO conc. up to 2% (with the O_2 content of the air at least 15%) offer the optimum range of usefulness.

47. STAMPE, G. and BANGERT, Fr. Behavior of the catalyst in the canister of the carbon monoxide gas mask. Z. ges. Schiess Sprengstoffw. 26: 24-26. 1931. C.A. 25: 2784. 1931.

In the CO mask the amount of carbon monoxide absorbed by the canister plays an insignificant part in its useful life, which depends in large measure upon the other foreign gases in the atm. It is especially sensitive to moisture and for this reason must contain a very efficient drying agent besides the catalyst (Hopcalite).

With an airflow of 30 l. per minute and a toxic concentration of 1 per cent by volume, the amounts of toxic gases in grams taken up by the Draeger canister and the breakpoints in minutes are as follows:

	g.	minutes
Phosgene	3.4	27
Cl_2	7.2	81
HCN	3.3	98
SO_2	18.5	232
H_2S	19.9	467
NH_3	2.3	108
CCl_4	8	41
C_6H_6	10	103

The effect of other gases in addition to CO was studied by passing a continuous air flow of 30 l. per min. through the canister. During the first hour CO (o.5 per cent by volume) and another toxic gas were added to the air stream, omitted for $\frac{1}{2}$ hour and added again. Results are shown in curves. The humidity was 30%.

48. TUTIYA, V.H. Catalytic decomposition of carbon monoxide. Inst. Phys. Chem. Res. Bul. 11:1136-1156. 1932.

Behaviour of molybdenum carbides.

49. VYAZOVYKH, B. Carbon monoxide as poison gas in time of war. Khimiya i Oborona 1938, No. 1, 15. C.A. 33:6469. 1939.

The gas masks absorbing CO contain:

activated charcoal satd. with $CuSO_4$	400 cc.
pure activated charcoal	200 "
pumice sat. with Na_2CO_3	200 "
$CaCl_2$	200 "
"Hotscalite"	200 "
(Oxides of Mn 50, Co 15 and Ag 5%)	

50. WEHRLI, S. Practical course in the chemistry of war gases.
            Protar 5: 57-61. 79-84. 1939.

        A section on CO is included.

51. WHITESELL, W.A. and J.C.W. FRAZER. Manganese dioxide in the
            catalytic oxidation of carbon monoxide. J. Am. Chem.
            Soc. 45: 2841-2851. 1923. C.A. 18: 613. 1923.

        The prep. of MnO_2 by methods which gave a product little
        contaminated by adsorbed alkali ($KMnO_4$ + cc.HNO_3,
        $MnSO_4$ + $KMnO_4$ in cc.HNO_3, treatment with conc. HNO_3 of
        MnO_2 prepared from $KMnO_4$ + H_2SO_4, oxidation of pptd.
        $Mn(OH)_2$) resulted in a material which was catalytic at
        temp. as low as -20°C. It was rapidly poisoned by H_2O
        but resumed its activity when the H_2O was removed by
        heating. CO_2 had no poisoning effect.

        It was suggested that the mechanism of oxidation of CO
        is (1) adsorption and oxidation, (2) desorption of CO_2,
        (3) reoxidation of catalyzer.

52. WILLIAMSON, Arthur G. Molecular and activated adsorption of
            carbon monoxide on manganous oxide (MnO) surfaces.
            J. Am. Chem. Soc. 54: 3159-3164. 1932. C.A. 26: 4993.
            1932.

        The adsorption of CO on MnO and MnO + Cr_2O_3 was measured
        from -190° to 444°. The adsorption has two forms:
        molecular at low temperature with a heat of adsorption
        of 1,000 to 2,000 cal., and an activated form noticeable
        above 0° causing a partial reduction of the catalyst.

53. WOLLIN, Karl. Use of the DEGEA carbon monoxide apparatus in gas
            plants. Gas und Wasserfach 72: 210-213. 1929. C.A. 23:
            2769. 1929.

        The canister incorporates a warning agent which gives
        warning of the approaching exhaustion of the active agent
        (metallic oxides). This mask can be used in atmospheres
        containing up to 1.8% CO and as low as 18.5% O.

54. WOLLIN, Karl. German gas masks for protection against carbon
            monoxide. Z. ges. Schiess Sprengstoffwesen 24: 30-32,
            71-73. 1930.

The catalyzer in the DEGEA mask consists of a mixture of Cu oxide and MnO_2 and contains a small quantity of calcium carbide, which generates C_2H_2 and acts as a warning agent when the catalyzer becomes ineffective by reason of excess moisture.

The mask is also effective against given amounts of phosgene, Cl, NH_3, SO_2, HCN and chloropicrin.

55. ZELDOWITSCH, J. On the mechanism of the catalytic oxidation of CO on MnO_2. Acta Physicochim. 1: 449-464. 1934.

A review of work done with S. Roginsky.

Normal molecules of CO and O_2 are adsorbed by MnO_2 at temperatures far below 0°C., normal CO_2 molecules are adsorbed even above room temperatures. Adsorption is practically instantaneous, and the temperature of the powder remains constant. Production of O_2 by MnO_2 or combination with O_2 is negligible at room temperatures.

When MnO_2 is at -21°C. or 0°C., activated adsorption occurs, accompanied by a rapid increase in temperature for a few minutes (20 to 30°C.). The increase in temperature corresponds to a heat of adsorption of 40 to 45 kg. cal. per mol and suggests that it is produced by oxidation of CO to CO_2 (41,000 kg.cal. per mol). The quantity of CO_2 that can be pumped off and frozen out is equal to the volume of CO that has disappeared.

The time required for the adsorption of one, two, etc. CC. (NPT) of CO, when CO_2 is not removed from the surface, increases geometrically so that $dq/dt = a(\exp) - a\,q.$

II. ADSORPTION OF CARBON MONOXIDE ON SOLIDS

(other than MnO_2)

56. BARRER, Richard M. The sorption of polar and non-polar gases
    by zeolites. Proc. Roy. Soc. A 167: 392-420. 1939.
    C.A. 33:4104. 1939.

    Adsorption isotherms for A, H_2, N_2 and He in the tempera-
ture range 62° to 384^OK showed that zeolites consisting
of three-dimensional networks such as chabasite and
analcite can adsorb enormous quantities of gas, the
adsorption of argon or hydrogen by chabasite being equal
in volume to the water vapour removed during the dehydra-
tion of the adsorbent.

    The fibrous zeolites natrolite and scolecite as well as
the laminar zeolite heulandite gave only slight adsorption.

    The calculated initial heat of adsorption for N_2 on
chabasite was 8800 cal./mol.gr., the largest reported van
der Waal's interaction energy for N_2.

    Dehydration of chabasite ($Ca_2Al_4Si_8O_{24}.12H_2O$) and analcite
($Na_{16}Al_{16}Si_{24}O_{96}.24H_2O$) was carried out in a vacuum for
several days at progressively increasing temperatures
reaching 480° on the last day for chabasite, and 330° for
analcite. The structure of these crystals does not
collapse when interstitial water is removed.

    At 89^OK the computed saturation values are 164 cc. N_2 at
N.P.T. per g. of original chabasite, at 194.5^OK it is
75.2 cc., for analcite 30.3 g. at 79.5^OK and 15.1 at
194.5^OK.

    The apparent saturation values fall off nearly linearly
with the absolute temperature.

    (Similar results might be expected with CO).

57. BEEBE, Ralph A. and Dennis A. Dowden. Heats of adsorption of
    gases on chromic oxide Cr_2O_3 at low temperatures. J. Am.
    Chem. Soc. 60: 2912-2922. 1938.

    As a result of numerous investigations on the adsorption
of gases on catalytically active solid surfaces, van der
Waals and activated adsorptions have become clearly
recognized as separate states of adsorption. Frequently
the two types occur in more or less well separated
temperature ranges, the activated type belonging to the
higher temperature.

    The heats of adsorption of A, H_2, CO, N_2 and O_2 on a
reduced chromic oxide surface indicate that all these
gases with the single exception of A, are in part held

in a state of activated adsorption, as well as in the van der Waals state, at temperatures as low as -183°C. In the experiments with CO, N_2 and O_2 the complex form of the time-temperature curves on a partially covered surface lead to the conclusion that the adsorbed gas changes over on the surface from an initial to a final activated adsorption.

Over 120 cc. CO are adsorbed without delay at pressures between 0 and 1.60 mm. at -183°C. on 12 g. of Cr_2O_3. The adsorbed carbon monoxide could be removed unchanged by evacuation at 400°.

Process A is rapid for all states of the surface and gives a heat of adsorption of 4 Cal.; process B is rapid for a bare surface but becomes slower for successive additions, and yields an additional 8 k cal.

At 0° the adsorptive capacity of Cr_2O_3 for CO, N_2 and O_2 is much less than at -183°; there is probably no van der Waals adsorption.

58. BENTON, Arthur F. Adsorption and solution of gases by metals. Trans. Faraday Soc. 28: 202-218. 1932. C.A. 26: 5241. 1932.

For CO on Cu adsorption is activated at 110° and physical (van der Waals) at -183°; at 110° the rate is so slow that equilibrium is not reached in 14 days.

On fused ferroferric oxide containing 0.15% Al_2O_3 the adsorption of CO is rapid at -183° but much slower at 0°. The nature of the slow process has not been ascertained.

Physical adsorption depends on van der Waals forces measurable by the b.p. or critical temp. and disappears about 200° above the b.p.

At -78.5°C. an active sample of copper (51.51 g.) adsorbs up to 17.5 cc. CO at 70 cm. Hg, a sample of iron (54.6 g.) prepared by reduction of fused ferro-ferric oxide (0.15% aluminium oxide) adsorbs about the same amount of CO at -183°.

(An earlier article by Benton in J. Amer. Chem. Soc. 45: 887-900. 1923).

59. BRADLEY, H. Theory of adsorption. Trans. Faraday Soc. 31: 1652-1655. 1935.

When v = gas vol. adsorbed in cc.
p = pressure in cm.
T = absolute temp.

a and b = const.
the adsorption of CO on coconut charcoal is

$$v = \frac{ap^{T/273}}{1+bp^{T/273}}$$

In all cases of adsorption of H_2O the temperature has to be halved.

60. BURSHTEIN, R., P. LEVIN and S. PETROV. Activated adsorption of gases on charcoal. Phys. Z. Sowjetunion 4: 197-211. 1933. C.A. 4: 197-211. 1933.

Between 20° and 400^OC. the difference in amount of CO adsorbed on ash-free charcoal and on the same charcoal containing 0.2% Pt is a positive constant with respect to temperature and pressure, and varies with the Pt content. Slow activated adsorption occurs for CO at 400°, the amount adsorbed being proportional to the square root of time.

61. BURWELL, Robert L. and TAYLOR, Hugh S. Activated adsorption of hydrogen and carbon monoxide - effect of water vapour. J. Am. Chem. Soc. 58: 1753-55. 1936. C.A. 30: 7954.1936.

H_2O vapour minimizes surface reduction of ZnO catalysts at lower temperatures. It is strongly adsorbed from gas mixtures by those fractions of the ZnO surface to which the gas mixture has access.

Satn. of ZnO surfaces by H_2O markedly inhibits the activated adsorption of H_2 and CO.

62. CARNER, W.E. and J. MAGGS. Adsorption of carbon monoxide on zinc oxide. Trans. Faraday Soc. 32: 174-178. 1936.

The heats of adsorption of CO on ZnO vary from 9.4 to 14.7 kg. cal. per mol. over the temperature range 195 to 318° K.

63. DOHSE, H. and L. MARK. Die adsorption von gasen und dämpfen an
festen oberflächen (Adsorption of gases and vapours on
solid surfaces). Leipzig. 1933.

64. DOWDEN, D.A. and W.E. GARNER. The heat of adsorption of gases
on chromium sesquioxide at low pressures and room tempera-
tures. J. Chem. Soc. 1939: 893-902. C.A. 33: 7185.1939.

The heat of adsorption of CO, CO_2, H_2 and O_2 on chromium
trioxide was measured at 18° for the oxide in an oxidized
and in a reduced state. The adsorbing surface was ten
times larger for the reduced than for the oxidized sub-
stance. The adsorption on an oxide surface of CO or H_2
is a two-stage process.

65. DURAU, F. and R. MULLER. The adsorption of gases on lead
chloride pellets. Z. anorg. allg. Chemie 232: 133-154.
1937.

The adsorption of nitrogen at pressures between 0 and 500
mm. is practically zero at $20^\circ C$. The adsorption of CO
is inferior to 0.05 cc. between 0 and 700 mm. and $20^\circ C$.
Less than 0.1% of the surface is covered with a mono-
molecular layer.

66. GARNER, W.E. and F.E.T. Kingman. Adsorption of hydrogen and
carbon monoxide on oxide catalysts. Nature 126: 352.
1930. C.A. 24: 5567. 1930.

H or CO adsorbed at room temperature on $ZnO-Cr_2O_3$
catalysts was given off at 100 to 120° but after 20 to 30
minutes was readsorbed on the surface of the catalysts.

On raising the temperature further no gas was given off
up to 350°, when H_2O or CO_2 was liberated.

67. GERSHENOVICH, M.S., G.F. DALETSKII and N.A. Kotelkov. Nichrome-
palladium as a new catalyst for oxidizing combustible
gases. Inst. recherches sci. union soc. croix rouge et
croissant rouge. C.A. 31: 8342. 1937.

Oxidized nichrome coated with Pd is a highly active
catalyst for the oxidation of CO and H_2.

68. HAYGARD, T. Basic magnesium carbonate as a promoter on a copper surface. J. Chem. Soc. 1932: 2055-2062. C.A. 26: 5823. 1932.

Adsorption isotherms at 20° were determined for H, N, CO, CH_4 and NH_3 on surfaces of Cu, Cu promoted with basic Mg carbonate and $MgCO_3$. The copper surface was prepared by reducing CuO mixed with $MgCO_3$ in H at 200°.

The promoter increases the area of the active surfaces.

69. HOMFRAY, I.F. Adsorption of gases by (cocoanut) charcoal. Zs. phys. Chemie 74: 129-201. 1910. Proc. Roy. Soc. (A) 84: 99-106. 1910.

At constant gas pressure up to 80 cm. the relation between temperature and concentration of the gas in the charcoal (3 g. in the experiments) is
$$-dC/dT = 2.303\ C/K$$
where T is the absolute temperature, $C = \dfrac{w100}{w + W}$ is the concentration of the gas expressed in g. gas in 100 g. (charcoal + gas) and K, is a constant. A concentration of 100% is taken as liquefaction of the gas.

(For CO the volume of gas absorbed is 24.0 at $227^{\circ}K$, and the value of K is 79.5 at $C = 1$ and $P = 5$ cm.

If y is the volume of gas adsorbed by 1 g.
$$\log y = \log \triangle 0 + \frac{\phi}{R} \cdot \frac{1}{T}$$
so that when log y is plotted as a function of 1/T a straight line is obtained that intersects the log y axis at the value $\triangle 0$, where 0 is the surface producing adsorption in one gram of the material and $\triangle$ the thickness of the adsorbing film ($\triangle / 2$ specific volume of adsorption). For CO the value of ϕ is 4,080 cal. per mole, and $\phi /R = 2,060$.

The specific volume of adsorption for charcoal is of the order of 10^{-2} cc. per g. coal, or about one-tenth of the space between grains).

Carbon monoxide (3g. charcoal, at 273°K)

(Volumes in cc. at 0° and 760 mm. Hg)

P	taken up (cc.)	not adsorbed (cc.)
0.6	18.57	0.07
3.0	51.66	0.40
7.5	79.63	1.03
17.3	105.43	2.38
34.7	134.05	4.78
66.7	165.0	9.20

In contact with a mixture of nitrogen and carbon monoxide the charcoal absorbs the gases in proportion to their concentrations.

(3g. charcoal)

P	T	V	not abs.	V absorbed	
cm Hg	abs.			observed	comp.
45.3	373	7.83	3.70	4.13	4.4
21.4	319.2	7.83	2.02	5.81	6.2
12.3	293	7.83	1.26	6.57	7.0
7.3	273	7.83	0.80	7.03	7.5
50.9	319.2	17.49	4.82	12.67	13.5
30.0	293	17.49	3.08	14.41	15.4
18.0	273	17.49	1.98	15.51	16.5
84.3	351	18.57	6.71	11.86	
18.3	273	18.57	1.73	16.84	
0.6	239.4	18.57	0.07	18.50	
85.6	293	41.70	8.78	19.01	20.2
etc.					

70. LANGMUIR, Irving Monolayers on solids (17th Faraday Lecture)
    Journal Chem. Soc. 511-543. 1940.

At sufficiently low temperatures the so-called permanent gases, hydrogen, nitrogen, argon etc., are adsorbed on surfaces by van der Waals forces. This kind of adsorption, which we shall call Type I, is characterized by rapidity and the relative ease with which saturation is attained.

When the temperature is raised this adsorbed gas evaporates, but in some cases at a much higher temperature it is slowly readsorbed. With this kind of activated adsorption it is almost impossible to reach definite saturation.

This distinction between van der Waals adsorption and activated adsorption was pointed out for the case of carbon monoxide on platinum (Langmuir, J. Amer. Chem. Soc. 40:1361 (esp.1399) 1918, Trans. Far. Soc. 17:607 1921). Taylor and others (J. Am. Chem. Soc. 53:578. 1931) have studied in detail many cases of activated adsorption.

From measurements of the adsorption of hydrogen by copper powder at temperatures from 25° to 200° C., Ward concludes that activated adsorption takes place in two distinct steps (Type II and III). Introduction of gas gave an almost instantaneous adsorption, (Type II) followed by a very slow adsorption (Type III) which increased in proportion to the square root of the time and depended only very slightly on the gas pressure.

Benton and White (J. Am. Chem. Soc. 52:2325-2336. 1930; 54:1373-1390. 1932) and Benton (Trans. Faraday Soc. 28:202-218. 1932) recognise these three types in interpreting experiments on the adsorption of hydrogen and carbon monoxide by powders of copper, iron, or nickel.

Taylor and Ogden (Trans. Faraday Soc. 30:1178-1190.1934), in studies of the rate of adsorption of hydrogen and carbon monoxide by zinc oxide, find an instantaneous adsorption, followed by a slow adsorption varying approximately with the square root of the time and not appreciably dependent on the pressure.

A study of the activated adsorption of CO on ZnO at temperatures of 184°C. and higher shows that concurrently with the activated adsorption some decomposition into CO_2 and C occurs. Carbon deposited on the catalyst is removed by H_2 at 184° and above, presumably CH_4 (Robert L. Burwell and Hugh L. Taylor, J. Am. Chem. Soc. 59:697-699. 1937).

71. MARKHAM, E.C. and Arthur F. Benton. The adsorption of gas mixtures by silica. J. Am. Chem. Soc. 53:497-507. 1931. C.A. 25:2039. 1931.

The adsorption of each gas in binary mixtures of CO and O_2 was measured at 1 atm. and temps. of 0° and 100°, and in mixtures of CO_2 with CO and with O_2 at 100°; the isotherms of the sep. gases were det. at the same temp.

Adsorption values calc. for the mixtures on the basis of a simple extension of Langmuir's theory of adsorption agree fairly well with abs. values for mixtures of CO_2 and O_2. In mixtures containing CO_2, however, the observed values are larger.

72. MOROZOV, N. M.   Kinetics of sorption processes. II Sorption
        of CO on bauxite. J. Phys. Chem. (USSR) 9:641-658,1937.
        C.A. 31:8303. 1937.   The sorption of CO by alumina:
        Acta Physicothim. U.R.S.S. 6:719-743. 1937.

73. MCKINNEY, Paul V.   Reduction of palladium oxide by carbon
        monoxide. J. Am. Chem. Soc. 54:4498-4504. 1932.
        C.A. 27:472. 1933.

        A slight initial reduction of 2.3g. PdO by a CO stream
        of 22.8 cc. per minute occurs at 23°. In the absence
        of O_2 none occurs below 76°. The reduction decreases
        in rate with time and does not go to completion below
        156°. $CO2$ in the CO inhibits reduction at 100° and
        retards complete reduction at 156°. O_2 accelerates
        the reduction; the reaction is complete at 76°.

74. MCKINNEY, Paul V.   The adsorption of gases on palladium
        oxide. J. Amer. Chem. Soc. 55: 3626-32. 1933.
        C.A. 27:5229. 1933.

        The adsorption of $CO2$ and of CO by PdO was measured
        ower the temperature range -78 to 218°. CO_2 adsorp-
        tion is of reversible physical type. CO shows physical
        adsorption at higher temperatures, the apparent
        maximum for activated adsorption at 350 mm. being at
        about 100°.

        The CO taken up during activation adsorption was re-
        coverable only as CO_2 for the most part.

75. NATTA, G. and E. CASAZZA   The activity of catalysts
        proposed for the synthesis of methanol. Giorn. chim.
        ind. e applicata 13:205-212. 1931. C.A. 26:80. 1931.

        The catalysts which show high CO_2 and CO absorption
        with low H_2 absorption, namely reduced $ZnCrO_4$ and
        4 ZnO + 1 Al_2O_3 are most effective. The absorption
        increases with increasing pressure up to 35 or 40
        atm.

76. NYROP, J.E.   Adsorption and catalysis. J. Phys. Chem.
        39:643-653. 1935.

        The adsorption of N_2, H_2, CO, H_2O on various metals and
        oxides and many catalytic hydrogenation, oxidation and
        hydration reactions that have been described in the
        literature are summarized and discussed.

77. REYERSON, L.H. and L. E. SWEARINGEN The adsorption of
gases by metallized silica gels. J. Phys. Chem.
31:88-101. 1927. C...21:845. 1927.

Adsorptions were measured for silica gel and silica
gel metallized with Ag, Cu, Pt and Pd, resp., and
isotherms obtained upon silvered gel at temperatures
between 0° and 218°.

CO and C_2H_4 were specifically adsorbed by all the
metallized gels except Cu. Per gram of adsorbent
silica gel takes up 1.60 cc. CO, silverized gel 2.75,
palladized gel 2.60 platinized 4.60, and copper gel 0.40.

78. SARTORI, Guido and U. FANO Adsorption of hydrogen, carbon
dioxide (carbon monoxide) and methanol on zinc oxide.
Gazz. chim. ital. 67:69-85. 1937.

Adsorption isotherms of H_2, CO, CO_2 and Me OH on ZnO
at 0°, 36°, 76°, 106° and 120^OC. Adsorption of H2 and
CO followed closely the Langmuir law.

79. SIHVONEN V. and U. HEMMING Carbon as an adsorbent
Suomen Kemistilehti 12B, 11 (1939) C.A. 33:8077. 1939

Initial adsorption on relatively inactive charcoals,
prepared from wood and sugar, of CO, CO_2 and H2O vapour
between -65 and 150 C., and pressures less than 300 mm.

80. TAYLOR, Hugh S. and Paul V. MCKINNEY Adsorption and
activation of CO at palladium surfaces. J. Am. Chem.
Soc. 53:3604-24. 1931. C.A. 25:5817. 1931.

The adsorption of CO by Pd from the oxide reduced by
H_2 at room temperature, was detd. at temp. from 86^OK
to 553^OK and pressures to 40 cm.

The isobaric curves show a mm. adsorption at 195^OK and
a max. at 273^OK. For the sintered samples the max.
occurs at 383^OK.

The rise in adsorption from 195^OK to 273^OK is an example
of activated adsorption.

81. TAYLOR, H.S. and G.B. KISTIAKOWSKY   Methanol catalysts.
         J. Am. Chem. Soc. 49:2468-76. 1927

         Adsorption of H, CO and CO$_2$ on ZnO and ZnO + Cr$_2$O$_3$
         were measured at 0° and 100°. Both these catalysts
         had adsorptive capacities considerably greater than
         those of most metal catalysts. The adsorption of
         both H and CO is large at very low pressures and
         rapidly reaches saturation.

         The surfaces have to be cleaned of H$_2$O and CO$_2$ by
         preliminary evacuation at 400°.

82. TAYLOR, Hugh S. and Geoffrey OGDEN   Trans. Faraday Soc.
         30:1178-1190. 1934.   C.A., 29:2418. 1935.

         A mixture of ZnO with excess of Mo oxide exhibits
         van der Waals adsorption in a low temperature range
         and activated adsorption in a high temperature range
         with both H and CO.

83. WAGNER, H.   Storage of carbon monoxide   Brennstoff Chemie
         12:87-89. 1931.

         Solubility of carbon monoxide at 100 atm. in organic
         solvents; adsorption of carbon monoxide by solid salts.