

ALIEN PROPERTY CUSTODIAN

PROCESS FOR CHEMICAL REACTIONS IN MELTS

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The present invention relates to improvements in carrying out reactions between gaseous or vaporous reactants.

This application is a continuation-in-part of our application S. N. 292,742, filed August 30, 1939.

It is an object of the invention to provide a process for carrying out reactions between gaseous or vaporous reactants wherein it is possible to control the temperature of the reaction very exactly.

In accordance with the present invention, the gaseous reactants are introduced into a molten bath, preferably a salt bath, and are maintained in such bath until the desired reaction is completed. The molten bath primarily serves as a heat exchanging medium, but also advantageously serves as a catalyst or a catalyst carrier. The reactants are preferably introduced into the molten bath in a finely divided form through nozzles in order that they thoroughly and uniformly intermix with the molten bath, and, also, in order that such gaseous reactants do not rise too rapidly through the molten bath and therefore escape therefrom before the reaction desired is achieved. The temperature of the molten bath is adjusted to the desired reaction temperature and is maintained at this temperature throughout the reaction.

It is possible in this manner to control the temperature of the reaction very exactly, even when the reaction carried out is highly exothermic and endothermic, as the molten bath possesses a high heat capacity. The thorough intermixture of the gaseous reactants and the molten bath constantly causes new heat exchange surfaces, and in catalytic reactions new catalytically active surfaces to be presented to the reactants.

It is necessary for the process in accordance with the present invention that the gaseous reactants are thoroughly intermixed with the molten bath in order that they remain thoroughly intermixed therewith until the desired reaction is achieved. Preferably the gaseous reactants are introduced into the melt in a finely divided condition and under such conditions that a thorough intermixture with the molten bath is achieved. In some instances it is desirable to enhance the agitating effect obtained by introducing an excess of one of the gaseous reactants or by introducing inert gases such as, for example, carbon dioxide, steam and the like, into the molten bath simultaneously with the gaseous reactants. The gaseous reactants are preferably introduced near the

bottom of the molten bath, and the depth of the molten bath is selected so that the desired reaction is completed before the reactants escape therefrom. Preferably, also, the reaction product as well as any unreacted reaction participants escaping from the molten bath are immediately cooled down to prevent undesirable reactions from taking place outside of the molten bath.

The process in accordance with the present invention is especially well suited for carrying out numerous types of reactions, such as, for example, hydration, dehydration, hydrogenation, dehydrogenation, oxidation, dissociation, polymerization and the like reactions. The present process is suitable for organic reactions in which, for example, hydrocarbons, alcohols, aldehydes, carboxylic acids, ketones, phenols, amines, may serve as gaseous reactants; and for reactions of inorganic nature, for instance, the production of hydrocyanic acid from carbon monoxide and ammonia or the production of sulfur trioxide from sulfur dioxide and oxygen.

Thorough investigations have shown that a considerable number of substances may be employed for the preparation of the molten baths employed in accordance with the present invention for example, nitrates, nitrites, chromates, acetates, chlorides, bromides, cyanides, cyanates, oxides, hydroxides, sulfates of alkali metals, alkaline earth metals, earth metals such as sodium, potassium, calcium, barium, aluminum and cerium. Furthermore, carbonates, phosphates, borates, silicates, glass or silica and organic compounds having high melting and boiling points such as urea, paraffin, naphthalene, decahydronaphthalene, halogenated naphthalenes, diphenyl oxide, nitrobenzene and the like may be employed for the preparation of the molten baths.

These compounds and substances may be employed either alone or in combination with each other. It has usually been found advantageous to combine several of the substances or compounds to form a mixture which is especially suitable for the desired reaction. Generally the composition of the molten bath is selected so that the temperature necessary for the desired reaction is approximately midway between the boiling point and the solidification point of the bath.

The following compositions have been found especially suitable for the molten baths. The temperatures recited are those for which the compositions are most suited. Of course, such baths are also desirable for reactions carried out at temperatures approximating these temperatures:

I. NITRATES

	° C.
30% KNO ₃ +70% LiNO ₃ -----	130
55% KNO ₃ +45% NaNO ₃ -----	218
50% KNO ₃ +50% NaNO ₃ -----	140
50% NaNO ₃ +50% NaNO ₂ -----	220

II. CHLORIDES

a

31% BaCl ₂ +48% CaCl ₂ +21% NaCl-----	430
50% BaCl ₂ +30% KCl+20% NaCl-----	540

b. Chlorides+carbonates

50% KCl+50% Na ₂ CO ₃ -----	560
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c. Chlorides+fluorides

85% CaCl ₂ +15% CaF ₂ -----	645
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d. Chlorides+sulfates

35% NaCl+65% Na ₂ SO ₄ -----	620
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e. Chlorides+phosphates

50% Na ₃ PO ₄ +50% KCl-----	680
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f. Chlorides+borates

88% BaCl ₂ +7% Na ₂ B ₄ O ₇ +5% MgO-----	980
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g. Chlorides+carbonates+sulfates

40% NaCl+20% Na ₂ CO ₃ +40% Na ₂ SO ₄ -----	500
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III. CHROMATES

50% K ₂ Cr ₂ O ₇ +50% Na ₂ Cr ₂ O ₇ -----	300
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IV. SULFATES

25% K ₂ SO ₄ +75% Na ₂ SO ₄ -----	830
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V. PHOSPHATES

70% Na ₄ P ₂ O ₇ +30% K ₄ P ₂ O ₇ -----	875
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44% K ₄ P ₂ O ₇ +56% KPO ₄ -----	615
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VI. SILICATES

45% BaSiO ₃ +55% Na ₂ SiO ₃ -----	905
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VII. BORATES

50% NaBO ₂ +50% LiBO ₂ -----	648
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VIII. BROMIDES

50% KBr+50% NaBr-----	640
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The molten baths employed in accordance with the present invention are maintained at the desired temperature by suitable heat exchange means. If the reaction being carried out is of endothermic nature, it is necessary to supply heat to the molten bath in order that the desired temperature be maintained for the reaction. This is preferably accomplished by internal heating of the molten bath. However, external heating may also be employed.

It has been found advantageous to employ flues or dipping burners for internal heating, the flues or burners preferably being arranged in a chamber adjacent to the reaction chamber so that the combustion gases do not mix with the reaction products. The molten baths may also be heated electrically, for example, by electric resistance heating or, if the bath is an electrolyte, by electrodes dipped therein. Also, in some instances it is possible to introduce the necessary heat into the molten bath by preheating the gaseous reaction compounds which are introduced or by introducing preheated inert gases into the molten bath. It is sometimes advantageous to combine various heating means, for example, employing dipping burners as the main supply of heat for the molten bath and employing electrode heating

to effect fine adjustment of the molten bath to the desired temperatures.

If the desired reaction is exothermic, it will be necessary that the heat liberated within the molten bath be withdrawn by suitable cooling surfaces.

Both in exothermic and endothermic reactions the temperature of the molten bath may easily be controlled thermostatically.

If the heating of the molten bath is effected with electrodes, the latter may also act catalytically or otherwise favorably affect the reaction. It has, for example, been found especially advantageous to employ graphite electrodes for heating the fused salt bath employed in the production of hydrocyanic acid from ammonia and carbon monoxide, as such electrodes deliver carbon monoxide as well as remove the undesired oxygen from the molten bath.

As has already been mentioned, the molten baths per se may serve as catalysts for the reaction carried out therein or they may contain suspended catalytic material. Certain oxidizing reactions may be improved by introducing boric acid, borates or barium compounds into the molten bath. On the other hand, catalytic materials which are insoluble in the molten bath may also be employed. Such insoluble catalysts are suspended within the molten bath in extremely finely powdered condition. Such catalysts which either tend to float or sink in the molten bath may be precipitated upon suitable solid carriers in order that the density of the composite catalytic material approximates that of the molten bath.

Various elements and compounds such as, for example, metals, metal compounds, earth acids or salts may be employed as catalysts. In hydrogenation reactions the usual hydrogenation catalysts may be employed such as nickel, iron, molybdenum, tungsten and zinc oxide. For oxidation reactions various known oxidation catalysts may be employed, for example, iron oxide and vanadic acid. Such dehydration catalysts as aluminum oxide, titanium dioxide, alkaline earth phosphates may be employed in facilitating dehydration reactions.

If the catalyst desired tends to sink in the molten bath employed, it may be deposited upon a light carrier, such as aluminum oxide, voluminous or active silica, asbestos, magnesium oxide, beryllium oxide, charcoal or activated charcoal. If the desired catalyst tends to float, it may be combined with relatively heavier carriers, for instance, heavy metals such as tungsten, copper and the like.

The process in accordance with the present invention is especially well suited for carrying through reactions which require high temperatures as well as for reactions which require that a constant temperature be maintained such as, for example, in the production of acetylene or ethylene from methane. The process in accordance with the present invention is furthermore especially well suited for carrying out partial oxidation reactions, such as, for example, the production of phthalic acid or maleic acid by the partial oxidation of aromatic hydrocarbons and the production of carboxylic acids, ketones, aldehydes or alcohols by the partial oxidation of methane or its homologues.

The process in accordance with the present invention may be carried out at normal, reduced or increased pressures, depending upon the requirements of the reaction carried out.

If substantial portions of the fused material of the molten bath are carried off in vapor form or as a mist together with the reaction products, these may be recovered in an absorption chamber.

The molten baths as well as catalysts contained therein may be easily regenerated during the process by passing a portion of the melt as well as any catalyst contained therein into a chamber adjacent to the reaction chamber wherein they may be subjected to a regenerating treatment, for example, with the aid of steam or oxidizing gases. Such regeneration treatment may be carried out continuously without interrupting the reaction carried out in the reaction chamber.

The following examples will serve to illustrate the present invention, but it is to be understood that the invention is in no way limited thereto.

EXAMPLE I

For the production of sulfur trioxide, dry roaster gases from pyrite furnaces containing about 7% of sulfur dioxide are introduced tangentially and counter-currently with an excess of air into a molten bath of 31 parts of barium chloride, 48 parts of calcium chloride and 21 parts of sodium chloride containing suspended silver vanadate as a catalyst. The molten bath is maintained at 480° C. by suitable heat exchange means.

The formation of sulfur trioxide is accompanied by a considerable evolution of heat and, at the same time, sulfur trioxide will decompose to sulfur dioxide and oxygen at temperatures

above 430° C. The use of a molten salt bath for the reaction is therefore of considerable importance as it is possible to regulate the temperature of the reaction within the molten bath very exactly. The yield of sulfur trioxide is at least 75% of the theoretical

EXAMPLE II

For the production of phthalic acid, naphthalene and an excess of air are injected into a molten bath of 31 parts barium chloride, 48 parts calcium chloride and 21 parts sodium chloride, in which vanadium pentoxide is suspended as a catalyst. The temperature of the molten bath is maintained at 480° C. The reaction product is rapidly cooled after egress from the molten bath, and phthalic acid is obtained in a yield of at least 90% of the theoretical.

EXAMPLE III

For the production of formaldehyde, air and an excess of methane are injected together with nitrous oxide gases in a proportion of 1 part nitrous oxide gases to 10 parts methane into a molten bath containing 50 parts NaBO₂ and 50 parts LiBO₂. The molten bath is maintained at 700° C. After egress from the melt, the reaction gases are passed into water whereby a formaldehyde yield of at least 70% of the theoretical calculated with reference to methane is obtained.

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