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Solid phase chemical reactions and new technologies

N S Enikolopov
Institute of Synthetic Polymeric Materials, Academy of Sciences of the USSR, Moscow

Principles for carrying out chemical reactions in solid bodies are considered in this paper as is the design of new technologies and materials based on the previously unknown phenomena which we discovered when studying reactions in the solid phase.

Modern chemical science has developed in the last 200–300 years on the basis of experiments performed while observing natural phenomena and appropriate special experiments. This knowledge became the basis of modern chemistry. However all the reactions which were observed in nature and studied under laboratory conditions proceeded mainly either in the gas or liquid phases or in solution, in melts or on the surface of a solid body. As a rule chemical reactions do not proceed or proceed extremely slowly in the bulk of a solid body because of the absence of diffusion of reactants to one another and diffusion of the reaction products. Alchemists even said that a solid body was death for chemistry since it had no motion. Several years ago we showed successfully that if a shear deformation was brought about in a solid body then at the point of shear deformation chemical reactions took place in it at extremely high rates. As is shown in Fig. 1, together with the shear stress τ there is also a certain pressure p applied to the substance being investigated in order that the system is not destroyed at the time of shear deformation. Before passing to a systematic presentation of the results of these experiments it is necessary to check that a shear deformation can be brought about in solid bodies in industry as under laboratory conditions.

Bridgman's anvil is shown in Fig. 2. The test sample (1), a substance or mixture of substances in which a chemical reaction is to be effected, is clamped between two anvils (2) of tempered steel. One of them (in the given case the lower) is rotated about its axis generating a shear deformation. This laboratory machine permits work with gram quantities. A similar shear deformation may be effected by pressing the solid test substance through a cone under high pressure (Fig. 3). Depending on the relationship $\lambda = S_1/S_2$ it is possible to vary the size of the shear deformation but the applied pressure p determines the rate of deformation. In this case it is possible to work with tens of grams of substance. There is also a series of other devices enabling experiments to be carried out under laboratory conditions. Industrial machines have been developed capable of processing tons of substance per hour. Extruders are such machines (Fig. 4). The rotating screw generates the required pressure and passes the substance into the gap formed between the stationary body of the extruder and the rotating bit of the screw. Two- and multiscrew extruders also exist where special 'cogs' effect shear deformation. At present tens of machines have been constructed in which solid phase chemical reactions can be effected under laboratory and industrial conditions.

The basic rules for carrying out solid phase chemical reactions are now considered. It has been shown that almost all reactions known in inorganic and organic chemistry will proceed under conditions of shear deformation in solid bodies. We have successfully studied hundreds of reactions such as polymerisation processes, addition, substitution and decomposition reactions, etc.

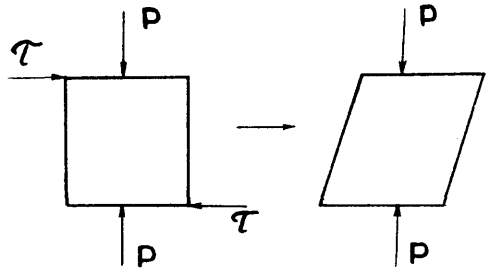


Figure 1. Schematic representation of the combined influence of pressure and shear deformation.

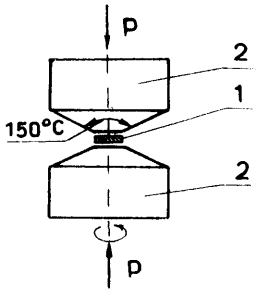


Figure 2. Bridgman's anvils.

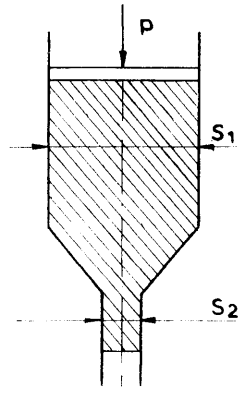


Figure 3. Outline of cone extruder.

A typical 'kinetic' curve of a solid phase reaction occurring under the action of shear deformation is shown in Fig. 5. In contrast to classical chemical kinetics the angle of rotation of the anvil and not

time is disposed on the abscissa, i.e. a value proportional to the shear deformation. The yield of product is on the ordinate as usual. All the chemical reactions studied by us proceed in accordance with the typical 'kinetic' curve.

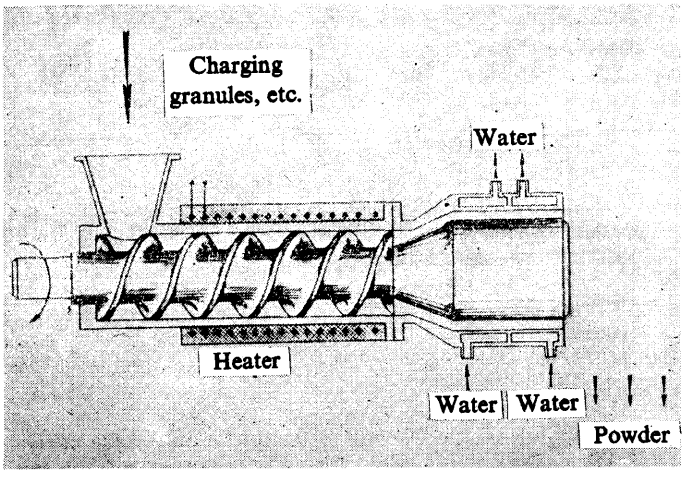


Figure 4. Extruder.

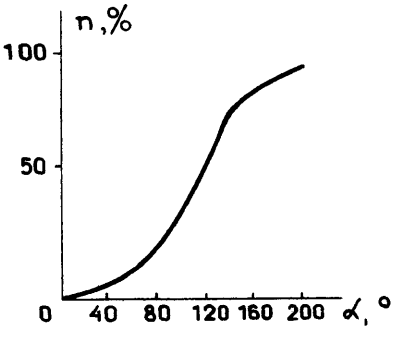


Figure 5. Dependence of polymer yield on the angle of rotation of the anvil (t = 20 °C, P = 10 kBar).

The most characteristic features of solid phase chemical reactions are as follows.

1. Simple compression of the sample by extremely high pressure does not induce a chemical reaction. After removing the shear deformation a long stay under high pressure also does not lead to an increase in product yield, i.e. there is no poste-effect. The direction of the deformation also does not influence the size of the yield. At a given value of deformation the yield will be the same independent of the rotation of the anvil to left or right or after many changes in the direction of rotation.

2. The rate of chemical conversion in solid bodies on shear deformation is extremely high in comparsion with the reaction rate in liquid and even more so than in the gas phase. Under isothermal conditions the reaction rate in a solid body is 3–8 orders of magnitude greater than in the liquid phase.

3. Under the conditions indicated the usual concept of 'catalysis' and 'catalyst' lose their classical sense. Reactions proceed without a catalyst although some special additives may influence the course of the process but this is an action on the mechanism.

4. The extent of chemical reaction is proportional only to the size of the shear deformation.

$$W = \frac{c_0 - c}{c_0} \sim \alpha,$$

where W is the extent of the reaction, α is the shear deformation, c_0 and c are the initial and running concentrations respectively.

The chemical reaction rate is proportional to the deformation rate.

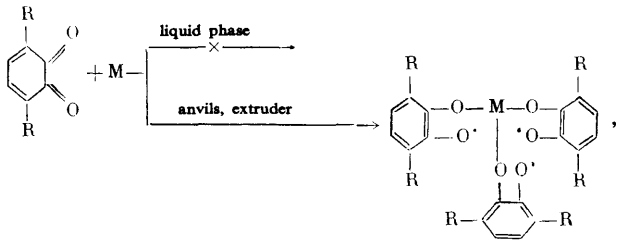
$$V \sim \frac{d\alpha}{dt}.$$

5. Mass transfer processes under the conditions indicated also have special features which are impossible to explain within the framework of the usual diffusion of molecules and atoms in solid bodies. Consequently it is impossible to use the generally accepted concept of a diffusion coefficient for the quantitative characterisation of the rate of mass transfer. Nonetheless using the concept of 'reduced diffusion coefficient' it is possible to compare the rate of mass transfer in a solid body at the point of shear deformation with the usual diffusion coefficient. It turned out that the value of the reduced diffusion 'coefficient' was 8–10 orders of magnitude greater than the diffusion coefficient in the same solid body without shear deformation and 3–5 orders of magnitude greater than the diffusion coefficient of the same molecules at the same temperature in the liquid phase.

The values given for the relative reaction rates and diffusion 'coefficients' were determined qualitatively and consequently are characterised by lower values. They may in fact be much greater. The reaction rate is determined as the total quantity of substance resulting from unit volume in unit time. However as was shown above the reaction rate is determined by the deformation rate and in the sample (tablet) being investigated the deformation rate varies from the centre to the periphery when rotating one of the anvils from zero to a maximum at the edge of the sample. Furthermore a large gradient in deformation rate is displayed across the thickness of the sample. Consequently the values given for the chemical reaction rate and the mass transfer rate represent only the lower limit of these values.

6. One of the main problems of chemical science is the determination of the course of a chemical reaction. Consequently it comprises many strictly established chemical rules specified thermodynamically or kinetically by the features of the chemical process. Numerous experiments by us have shown that these laws and empirical rules of conducting chemical reactions, which have been discovered when investigating processes in liquid and gaseous phases, are very frequently also displayed in the solid phase. There are several cases when a reaction does not proceed in a solid body as predicted by classical chemistry. For example quinone reacts with

powdered metals (aluminium, chromium, iron, etc.) and forms a free radical with three unpaired electrons:



where R = $C(CH_3)_3$; M = Al, Cr, V, Mo, etc. Evidently the analogous reaction does not proceed in the liquid phase by virtue of the fact that an aluminium atom is not able to lose 3 electrons sequentially and quadrimolecular reactions are never observed in chemical kinetics.

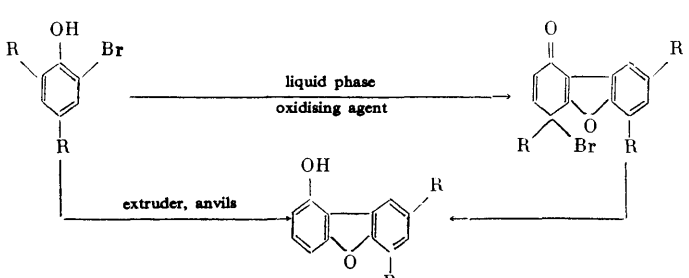
7. In solid phase chemical reactions, as a rule, there are few intermediate reaction products (the final product is generally formed straight away). In the liquid phase

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C \ldots \xrightarrow{K_n} X,$$

and in the solid phase A → X where K_i is the rate constant.

This is linked with the fact that the time for carrying out a chemical experiment is comparable with the time characteristics of the sequential intermediate reactions ($\tau = 1/K_i$). It is evident that in the liquid phase all the intermediate products (B, C, etc.) disappear after a long time and only the final product remains in the system.

8. In the solid phase the reaction rate constant is several orders of magnitude greater than in the liquid phase. Consequently in the latter case the characteristic reaction time becomes much less than the time of the experiment and the formation of only the final reaction product is observed. One of such cases is shown below when the formation of an intermediate was not observed on carrying out the reaction in the solid phase.



where R = t-Bu.

9. The rates of chemical, metallurgical, biological, enzymic and other processes depend on temperature and as a rule the reaction rate grows as the temperature is increased (Arrhenius rule):

$$V \sim e^{-E/kT},$$

where E is the energy of activation.

The size of the energy of activation (it may have a value of a few to tens of kilojoules per mole) characterises the rate of increase of reaction rate with rise in temperature. That is why some processes accelerate rapidly and others less so with increase in temperature. As a rule however all accelerate.

It turns out that in solid phase chemical reactions occurring under the action of shear deformation the activation energy is zero. Reaction rates do not depend on temperature in the temperature range from −196 to +200 °C. This is a characteristic of numerous reactions, such as addition, dissociation, substitution, polymerisation, etc. It is necessary to record specially that in solid phase chemical reactions the energies of activation are zero not only in exothermic but also in endothermic processes. The absence of activation energy in exothermic reactions is explained by the reacting molecules being deformed in the pliable deformation of a solid body. These deformed molecules or combinations of deformed molecules already have sufficient energy to surmount the kinetic barrier (ε) (Fig. 6). But in the case of endothermic processes, in addition to the kinetic barrier, a barrier exists linked with the size of the dissociation energy (Q). The overall energy equation is

$$E = \varepsilon + Q.$$

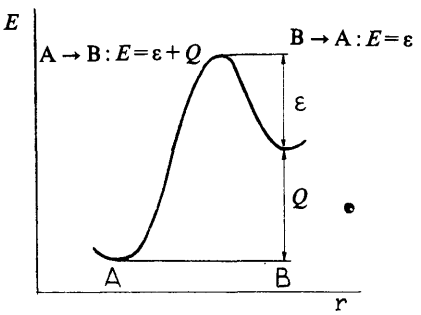


Figure 6. Dependence of the potential energy of the system along the reaction coordinate.

In solid phase endothermic reactions the energy of activation is also zero. This indicates unequivocally that among the deformed molecules (excited as a result of elastic deformation) or combination of molecules there are some in which the accumulation of total energy is greater than ε + Q. It is evident that the number of these molecules is not great since it is difficult to accumulate a large quantity of energy in the system because of the incompressibility of solid bodies at moderate pressures (tens of kilobars). That is why the extent of reaction in endothermic processes is insignificant.

It is therefore seen that the absence of an energy of activation in solid phase chemical reactions is a very important feature. It was shown by special experiment that this phenomenon is not linked with local heating in a friable solid body at the time of deformation. The portion of the volume being heated is too small to explain the absence of an energy of activation within the framework of these concepts.

As has been shown the rate of a solid phase chemical reaction is proportional to the deformation rate. Industrial machinery and laboratory equipment have upper limits for rates of deformation consequently they also have an upper limit for reaction rate. As indicated these rates are 5−8 orders of magnitude greater than the rates of these reactions in the liquid phase. It is evident that if the deformation rate can be successfully increased it should be possible to bring about solid phase chemical reactions at even greater rates than those indicated above.

About 50 years ago Bridgman showed that if a solid body or powder is pressed between two anvils then the system loses mechanical stability above a certain critical pressure and is destroyed with scattering of the solid particles. Our investigation showed that the critical pressure for bursting depends on many factors particularly on the thickness of the tablet being tested (h) (Fig. 7). It turned out that a minimum value of h_{cr} exists below which the system does not burst even at very high pressures (maximum pressure was 30 GPa in the case in question). However h_{cr} is not a strictly limiting value. If there is shear deformation as well as pressure then the system loses mechanical stability at a thickness lower than h_{cr}. In this case a thickness (h_{cr}^{o}) exists at which even a shear deformation does not lead to bursting. It turns out that the critical bursting pressure also depends on the diameter and mass of a tablet, the rate of loading the system, the nature of the substance, small additions and many other factors apart from the tablet thickness. Thus above the continuous curve (Fig. 7) the system is mechanically extremely unstable and leads to bursting, but below the curve it is stable.

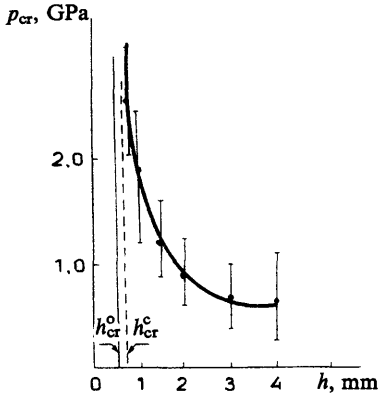


Figure 7. Dependence of critical explosion pressure p_{cr} on tablet thickness.

Our qualitative investigations showed that the duration of these bursts was much less than 10^{-5} to 10^{-6} sec (it is possible that the real time was less than 10^{-8} and 10^{-9} sec).

The investigations showed that under the indicated conditions the same reactions take place as under the action of shear deformation but their time course was not seconds or tens of seconds but less than 10^{-6} sec. This is like the so-called detonation reactions when the rate of propagation of the chemical reaction is greater than or equal to the rate of propagation of sound in the same solid body. Evidently simple long term compression without mechanical bursting (below the lower continuous curve in Fig. 7) does not lead to chemical reaction.

Endothermic reactions occur on mechanical bursting because mechanical energy accumulates in a solid body on compression (possibly in the experimental equipment generally) and this mechanical energy is transformed directly into chemical energy. As is seen from Table 1 the limit (critical bursting pressure p_{cr}) does not depend on temperature in the range −78 to +80 °C.

The reaction yield also does not vary. As was shown above the yield in endothermic reactions is naturally so low because the energy stored in the system is also little. So long as a reaction is weakly exothermic, such as hydrolysis and neutralisation reactions (see below), then after the same time of bursting (10^{-6} sec) the yield is almost 100%. This is linked with the fact that there is no need to put additional energy into the system while carrying out the reaction, on the other hand energy, although little, is evolved. It is only necessary to overcome the kinetic barrier which, as has been shown, does not exist in solid phase reactions.

Table 1. Bursting reactions.

Substance	Bursting pressure, 10^2 MPa		
	−78° C	room temperature	80° C
$CuSO_4 \cdot 5H_2O$	7.5	7.5	7.0
$CuCl_2 \cdot 2H_2O$	15	8	7.5
$Na_2SO_4 \cdot 10H_2O$	3	3	− *
$Na_2CO_3 \cdot 10H_2O$	4	4	− *
$MnSO_4 \cdot 5H_2O$	7	7	7
$ZnSO_4 \cdot 7H_2O$	11	9	6
$NiSO_4 \cdot 7H_2O$	9	10	5.5
$CoSO_4 \cdot 7H_2O$	7	6	4.5
$FeSO_4 \cdot 7H_2O$	11	13	15
$MgSO_4 \cdot 7H_2O$	7.5	9.5	− **
$Al(NO_3)_3 \cdot 9H_2O$	8.5	3.5	− *
$KAl(SO_4)_2 \cdot 12H_2O$	7	6.5	5
$Cr_2(SO_4)_3 \cdot 6H_2O$	17	17	−***
$KCr(SO_4)_2 \cdot 12H_2O$	13	17	8
$(NH_3)_2Fe(SO_4)_2 \cdot 6H_2O$	8	5	5

* No burst, sample was irrigated.
** Two sequential bursts at pressures of 3 and $15 \cdot 10^2$ MPa.
*** Burst occurs only on dropping pressure.

In the case of strongly exothermic reactions (a heat effect for the reaction amounting to hundreds or thousands of kilojoules) in addition to a detonation rate for the course of the reaction the formation is observed of a shock wave leading to destruction of the anvils and most of the experimental equipment. Metallothermic reactions are such reactions when one metal by virtue of its own high reactivity reacts with oxides, sulphides or sulphates of another metal and replaces it.

$$M^1 + M^2(X) - M^1(X) + M^2,$$

where X is $(O)_n$, $(S)_m$ or $(SO_4^{2-})_u$, etc. (n, m, u are integers).

An enormous quantity of non-ferrous and rare elements are produced by means of metallothermy at the present time. This industry has developed successfully at home and abroad for more than ten years. The mechanism and kinetics of these reactions are consequently well known.

The characteristic feature of metallothermic reactions is that they are, as a rule, strongly exothermic. The reactions shown below are also extremely exothermic.

$$CuSO_4 + Al \rightarrow ?$$
$$CuSO_4 + Mg \rightarrow ?$$
$$Fe_2O_3 + Al \rightarrow ?$$
$$Fe_2O_3 + Mg \rightarrow ?$$

The composition and quantities of the reaction products are still not strictly established.

Under uniaxial compression of mixtures of these powders (particle size from 0.1 to 1 mm) at room temperature the system loses mechanical stability (explosion) at the point of reaching a pressure equal to p_{cr} and as a result of the vigorous reaction a detonation occurs with destruction not only of the anvils but also of most of the equipment. It must be noted that each detonation leads to the destruction and scattering of reaction products which markedly hinders investigation of them.

Metallothermic reactions have been studied in a detailed manner by scientists all over the world for over a hundred years. It has been established that under the usual conditions the reaction is initiated at 1100–1200 °C and spreads at a rate of millimetres per second. The temperature at the spreading front of an exothermic reaction is 2000–2500 °C.

In the present case reaction is initiated at room temperature and is complete after less than 10^{-6} sec, consequently the propagation rate is kilometres per second. It must be noted particularly that although the dimensions of the reacting solid particles are comparatively large (diameter ~1 mm) the reaction successfully reaches an advanced stage of completion after so short a time.

Combination of the results obtained indicates that in the given case the detonation course of the chemical reactions occurs not as a result of high temperatures with subsequent heating of the unreacted layer as happens on thermal spreading but isothermally at low temperature like the usual solid phase chemical reaction, a significant portion of the thermal energy is evolved after completion of the reaction.

In the case of strongly exothermic reactions (metallothermic for example) the time for completion of the process is less than 10^{-5} to 10^{-6} sec. The propagation rate will be of the order of kilometres per second (anvil diameter 1 cm) and not millimetres per second as in thermal propagation. On the other hand the proceeding of a solid phase chemical reaction at detonation rate, isothermally, at low temperatures shows unequivocally that in solid phase reactions a mechanism exists for an ultra high speed process without initial heating up of the system, i.e. not linked with the Arrhenius rule. This is also indicated by the fact that in the reactions investigated the sizes of the reacting particles were of the order of 1 mm but the reaction went to completion. Complete conversion of the system at the molecular level had occurred after a time of less than 10^{-5} to 10^{-6} sec.

The detonation course of metallothermic reactions in solid bodies is accompanied by destruction of the anvils and of the equipment generally. This indicates that under the given conditions a mechanism exists for the transformation of chemical energy (reaction thermal effect) directly into mechanical energy without high temperatures and without the formation of a gaseous phase.

The conversion of the chemical energy of a reaction into mechanical is usually effected in the following manner. In a closed volume in the gas phase or under conditions when a gas phase is formed, the thermal energy evolved as a result of a chemical reaction heats the system, the pressure in the system rises enabling mechanical work to be carried out. In the case of solid phase chemical reactions it is seemingly necessary to assume formation of a shock wave directly at the time of the process. As was shown above in the case of decomposition (endothermic process) the reverse process occurs, mechanical energy is converted directly into chemical energy without initial heating of the system.

Let us consider the possibility of using the results obtained from investigating solid phase chemical reactions such as the higher mixing rate (diffusion 'coefficient') in comparison with liquid phase reactions, the independence of the rate of chemical conversion on temperature, the absence of catalysts, etc., in the technology of manufacture of useful substances and materials.

In modern industry (chemical, metallurgical, building materials, cellulose–paper, etc.) enormous quantities of solvent and catalyst are used for the optimum conduct of a process in the liquid phase and processes are carried out at extremely high temperatures. The need to use solvents, catalysts and high temperatures becomes superfluous for a solid phase process.

Investigations have shown that the known industrial processes may be carried out at room temperature without using solvents. The manufacture of soap has been known to man from ancient times. The process reduces to the addition of water to solid fat and solid ash and the mixture is boiled to form soap. Soap is manufactured by this technology up to the present the only difference being that solid alkali is used in place of ash. We have developed an industrial method of soap manufacture in a solid phase without solvent. At the present time a dry method of making paper from wood pulp has been developed similarly.

On the basis of the ideas described above a new physical elastic deformation method of crushing has been developed. It must be noted that contemporary crushing machines (ball mills, vibration mills, disintegrators, etc.) have an extremely low performance. When crushing synthetic and natural polymers (resins, wood, polymers, cellulose, etc.) by the elastic deformation method performance is increased by more than an order of magnitude.

Mixtures rather than individual polymers are widely used in industry at the present time to obtain new materials and articles made of them. Usually two basic methods are used. These are fusing and mixing or precipitation from a common solvent. Both methods have several technical, economic and qualitative drawbacks.

As has been shown the rate of mixing is sharply increased in the solid state on shear deformation. The very same occurs with macromolecules. Consequently a new technology for obtaining polymeric mixtures has been successfully created.

The use of solid phase chemical processes in industry may therefore lead to the creation of new, ecologically clean and energetically advantageous processes.