SOME ASPECTS OF CHEMICAL ENERGY IN GEOLOGY.

by

VINCENT ALEXANDER SAULL

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Signature of Author ______________________________
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Certified by ______________________________
Thesis Supervisor

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Chairman, Departmental Committee on Graduate Students

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"Some Aspects of Chemical Energy in Geology."

by Vincent Alexander Saull.

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ABSTRACT.

Every physico-chemical transformation involves a redistribution of energy, with concomitant production or absorption of heat. This paper is a discussion of the nature and significance of the chemical energy associated with certain geologic reactions, and of the heat effect.

The origin of the energy involved in igneous and metamorphic activity is one of the major unsolved problems of geology. Heretofore, primary heat, and heat due to radioactivity or friction have been suggested as agents. No unified treatment of the chemical factor has appeared.

Tendency towards chemical transformation is due to thermodynamic instability. This instability can be predicted from knowledge of the thermodynamic properties of the system concerned. Realization of any particular reaction, however, is conditioned by the rate at which it proceeds.

Reactive materials can be effective as heat sources in metamorphism only if the reaction rates concerned are sufficiently slow relative to the rate at which the material is brought into the metamorphic region. That is, in the case of sedimentary material, if the reaction rate is slow relative to the rate of deposition.

On theoretical grounds, and from such data as are available, it is apparent that many metamorphic reactions are exothermic. It is suggested that much of the geologic tradition of endothermic reactions in metamorphism stems from a confusion of the heat required to accelerate an already spontaneous reaction, and that required to initiate the reaction tendency itself.

From the data, it appears that certain geologically important reactions can develop, under adiabatic conditions, temperature rises of several hundred degrees Centigrade. On the basis of such results, it is suggested that granitization is a sort of spontaneous combustion, the initiation and character of which depends on local chemical, mechanical, and thermal factors.

The significance of the general theme for several aspects of geology is discussed. A mathematical expression of the problem is given, and the possibility of obtaining useful solutions considered.

Thesis Supervisor:
Dr. Norman Haskell.

Introduction.

This paper is an attempt to outline certain aspects of the role of chemical energyin geology, with the aim of stimulating more general consideration of this factor.

Briefly, the problem is as follows. All physico-chemical transformations invalve either production or absorption of heat locally. Now, other parameters remaining constant, the rates of such transformations are temperature-dependent. Thus, in a region experiencing energy transformations of this sort, the temperature is the result of a complex interplay of transformation energy, rate of transformation, and heat dissipation, all in accordance with the heat flow equation. It is this interplay, its origin, nature, and geologic application, that comprise the subject matter of the paper.

As will be brought out in the text, there is a lack of exact experimental data relevant to the problem. In this situation, the aim has been to stress basic principles, rather than risk prejudicing the general theme by over-enthusiastic use of such data as are available.

I. THE ENERGY PROBLEM IN GEOLOGY.

a. Importance of the problem.

The question of energy economy is fundamental to a large number of geologic problems, and implicit in many others.

A few such problems are those of metamorphism, orogeny, vulcanism, ore deposition, and cosmology. Similar energy considerations arise even in biophysical and weathering processes, though less naturally.

The above situation is perhaps not remarkable, since energy balance is an attribute of every physical process. What is surprising, however, is our general inability to resolve satisfactorily the problem of energy balance, which usually reduces to that of finding an adequate energy source.

This basic weakness is nowhere more striking than in petrology. The following quotations are from Turner and Verhoogen (116, p. 352).

> "Probably the most important geophysical problem confronting the petrologist concerns the determination of the distribution of temperature in the earth. .... Heat is undoubtedly the driving factor behind many, if not all, internal geologic phenomena. Problems concerning sources of heat and the temperature distribution are thus among the most fundamental, but unfortunately among the most elusive, in the realm of geology. .... The problem of the igneous petrologists is therefore to find an adequate mechanism by which comparatively insignificant amounts of heat may become focussed on rather small portions of the earth's crust in order to raise the temperature locally as much as several hundred degrees."

The critical role occupied by petrology in geology as a whole has been established over several centuries of observation. Thus from this point of view alone the energy question is of fundamental interest.

With respect to the broader problem of the heat economy of the earth as a whole, Van Orstrand (117, p. 125), writes:

> "A vast amount of research has been devoted to this subject, but the fact remains that the origin and maintenance of the earth's internal heat continue to be one of the outstanding unsolved problems of science" (sic).

b. Sources of energy in geology.

The following table presents a list of energy sources which may be geologically effective, together with a tentative indication of their spheres of importance.

TABLE I

Source	Effect		
	Surface	Crustal layers	Infra-crustal
Primary heat	nil	probably nil	Probable
Radioactivity	nil	present	probable
Chemical energy	present	present	probable
Cosmic radiation	present	present	nil
Solar radiation	present	nil	nil
Friction	present	present	present

Of these sources, primary heat and radioactivity may be termed the "classical" ones, in that they have received by far the greatest amount of attention in the literature. However, these sources are certainly not the only ones operative, and the true nature of their geologic contribution is quite uncertain. In this situation, it is advisable to review briefly the whole question of the nature of the energy sources locally important in the earth.

The problem is to evaluate the effect of the above sources relative to one another, and to what is known of the geology of each of the earth-regions given above. With respect to the latter, the writer feels that consideration of the geology of the environment is quite basic to any intelligent discussion of the subject.

1. Primary heat flow.

This is the most venerable of the sources listed, and has received attention since at least the days of Laplace. Nevertheless, absolutely nothing is known with certainty of the nature of this heat, or even of its existence. The idea of a hot interior for the earth was, in the past, based upon the visual evidence of volcanoes, and observations of terrestrial temperature gradients. Nowadays, there is abundant geological evidence that such phenomena by no means necessarily imply the presence of a primary heat flow. Such evidence is primarily: the localization of heat effects at the surface, and the presence of heat sources in the mantle which are qualitatively capable of causing the observed effects. It is not even certain that the origin of the earth involved any high temperature phase.

In any case, direct observation of primary heat is impossible, because of the presence of the crustal layers, with their definitely established contribution. The most logical approach is to consider whether agencies about which we do have definite information are able to explain the observed features. Then we shall be able to judge the probable nature of the primary effect.

2. Radioactivity.

Radioactivity, discovered in 1898, was suggested as a source of geologic heat as early as 1903, by Joly (51). This prompt application of physics to geology was due primarily to the existence of the spirited controversy then raging over the validity of Kelvin's figure for the age of the earth.

The general order of magnitude of the radioactive content of the various rocks is now known, for the crustal layers at least. Radioactivity in the mantle and core is uncertain, but measurements on meteorites, and geochemical predictions, may throw light on the matter. Besides the elements now known to be radioactive by laboratory measurement, there may exist other longer-lived radioactive elements, which by their abundance are important. Since these may be beyond direct experimental detection, theoretical predictions from nuclear structure, or from geologic measurements in favourable localities, may provide the only clue to their existence. Further, there is the possibility of radioactivity and fission caused by cosmic radiation being important.

Finally, the very basis of the heat production process is being investigated, and it is apparent that some of the radioactive energy goes into disruption of mineral structure, at least initially.(99).

The above sketch should indicate that the radioactivity question is still very much alive, and that a comprehensive treatment of the geologic relations has yet to be produced. As far as current geologic opinion is concerned, radioactivity has, with few exceptions, been considered as only a secondary source of heat, where problems of petrology are involved. There is, however, the "blister" hypothesis of Wolfe (125). (For such broader problems as the heat economy of the bulk earth, convection and the like, radioactivity has of course been considered a prime agent.)

3. Chemical Energy

Every chemical reaction involves redistribution of energy, and local production or absorption of heat. The general nature and importance of geologic reactions is well known. These are, first, the reactions of the weathering zone, intimately connected with meteorological reactions, and the process of which is continually before us. Then there are the metamorphic reactions, of the zone of anamorphism, which are mostly deduced from a knowledge of the original rock constitution, texture, and fabric. The precise conditions under which these reactions have occurred, and their rates, are uncertain. However, that they have occurred, and in finite time, is beyond doubt.

Thirdly, there is the possibility of reactions located in the mantle or core. There is little direct evidence of this, but also none in refutation of their existence. Philosophically, it would seem that such must exist. Otherwise, we are bound to consider the interior of the earth as everywhere in equilibrium. This is difficult to imagine, no matter what theory of origin of the earth we favour. It is also against the seismic evidence of deep earthquakes, and such evidence as supports the existence of convection currents. These reactions may amount to mere phase changes on cooling, or may be part of an involved and vigorous restoration of equilibrium. The possibility of phase changes within the mantle has been discussed by Bridgman (10B).

Objectively, chemical energy has many of the features required of a geological source, for example the possibility of extreme VARIATION IN intensity and distribution.

4. Cosmic radiation

In magnitude, the energy presently impinging on the earth in the form of cosmic radiation is but a small fraction of the generally accepted outward heat flux of the earth. Very rough calculations from such data as given by Greisen (39), indicate that this fraction is of the general order of 10^{-12}. Hence on a simple energy exchange basis, cosmic radiation seems to be of no interest.

However, because of the interesting indirect effects which radiation may initiate, which effects can be related also to radioactivity, some discussion of cosmic radiation is useful. This is particularly so since cosmic effects have rarely if ever been discussed in the geologic literature. (An exception to this last statement might be the geological application of the radioactivity of C^{14}, which isotope apparently owes its present existence to cosmic radiation.)

The general effects of radiation on solids have been discussed by Slater (99), and by Richtmeyer and Kennard (89, p. 701). Much of the interest of practical physicists in the effects of radiation on solids is due to the destructive thermal and mechanical effects which refractories exposed to radiation may undergo. Radiation effects are conveniently divided into effects on the electronic structure and effects on the nuclear structure.

Charged particles in the electronic region may be accelerated by the electronic and nuclear fields, and lose energy by radiation. At the same time, the electronic equilibrium is disrupted, resulting in ionization, and perhaps in the creation or destruction of chemical bonds between adjacent molecules. For most substances, the rate of restoration of equilibrium to the electronic structure is very rapid, and disturbance of this sort disappears as heat. For insulators, there is less mobility of the electrons, and electronic disturbances may be to some extent "frozen in". This appears to be the origin of the darkening of certain leucocratic minerals in radioactive pegmatities. As far as chemical reactions are concerned, molecules in favorable orientation might be affected by electronic changes, but for solid state reactions, the rate-determining step is usually the diffusion of particles to contiguity, and effects should be negligible. In other reactions, such electronic excitement could have a definite catalytic effect.

Effects on the nucleus are more important insofar as structural change is concerned. The physical properties of solids are conditioned almost entirely by the positions of the nuclei, and as mentioned, it is the displacement of the atoms as a whole, and therefore of the nuclei, that is the basic feature of solid state reactions. The particles which are able to affect the nucleus are thus of prime interest. These are the high momentum particles, as neutrons and mesons, and the heavier charged particles such as alpha particles and fission fragments. Gamma rays and beta particles can produce effects which are of ionizing character only.

Details cannot be discussed here, but nuclei may be effected by mere collisional displacement, or nuclear reactions may be stimulated. Effects are conditioned to a large extent by the speed of the particles involved. For charged particles, at high speeds energy loss is primarily by ionization, while at lower speeds, atomic displacement is the rule. This is also so for neutrons. However, for mesons, George (30) gives the following formula for the energy loss of mesons with depth:

$$\frac{dE}{dx} = a + bE + c \ln E$$

(a, b, c, are constants, E = energy, x = depth)

The constant term is ionization loss, the linear term loss by nuclear excitation and nuclear reaction, and the logarithmic term loss by Cerenkov radiation. Above 100 BeV the linear term dominates, that is, nuclear effects dominate above that energy.

Structural effects due to radioactivity are evidenced in the frequent development of the metamict state in radioactive minerals. Radioactive haloes generally show maximum blackening over one or more radii, which is probably due to the above-mentioned speed effect. The important point for this paper is that at least some of the radiation energy goes into structural damage, and not directly into heat.

The effects of cosmic radiation are of course decidely limited by the small total energy available, as mentioned above. The interesting feature is the high penetrating power of some of the particles. A very small number of observations have been made on cosmic particles underground (George 30), but fast particles have been determined at 3000 meters, and must penetrate even further. The intensity at this depth is however only 3 x 10^{-6} of the sea level intensity for the experiment in question. The effect then, of cosmic radiation, is a small amount of direct heating, and a similarly small number of nuclear interactions. With regard to these latter, some may be fissions, in which quantities of energy much greater than that of the particle itself may be triggered. Some will involve nuclear displacements, and others the development of radioactive isotopes, which again may develop eventually more than the input energy. The upshot of this is that cosmic radiation should be borne in mind as a possible explanation of some very local effects, and new developments in knowledge of the radiation should be applied to geology as soon as possible.

5. Solar Radiation

The pre-eminent role played by solar radiation in biology, meteorology, and related sciences is well known. It is not too much to say that all surface processes are tuned to solar radiation. In amount, the energy received from the sun is several orders of magnitude greater than that conducted outward from the earth. Geiger (31) gives data from which this amount may be estimated. Thus, at the upper limit of the atmosphere, the vertical flux is about 2 calories per minute per square centimeter. This vertical incidence occurs only in the neighbourhood of the equator, of course. Averaging over all latitudes, the flux can easily be shown to be about 1/2 calorie per minute per square centimeter. The albedo of the earth varies from place to place, with surface conditions and weather. At European latitudes Geiger states it to be 0.42. That is, 42% of the incoming radiation is reflected back to space. Van Orstrand (117) cites a value 0.29. In any case, the average heat flux is about 1/4 calorie per square centimeter per minute, or about .004 calories per second. Taking the outward heat flux from the earth to be about a micro-calorie per second per square centimeter, we have the above-stated relation. Local variations in albedo, seasonal variations at any particular point, and, of course, latitude, will affect the figures, but not as much as an order of magnitude.

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It is clear that if the earth receives a net amount of heat yearly, surface processes must be on the whole endothermic, if the earth is not to heat up continually. There is of course good geological evidence that there have not been extreme variations in temperature over the average of geological time. The tracing through of the energy economy of the surface would be of extreme interest in geology, and a fairly good picture could probably be achieved with data presently available. This cannot be done here, but it is obvious that, since the weather cycles involve little energy change, much of the surplus energy may appear as chemical energy in sediments.

Meteorological studies on this point do not offer much of a positive nature. The processes involved are extremely complex, and there is also an insufficiency of data even on those processes which are relatively well understood. The meteorological approach is, in the present state of affairs, to use the fact that climate has not varied essentially throughout geologic time, and then to calculate the missing radiation-back-to-space parameters on this basis. Possibly, detailed analysis of the data on hand could go further.

The writer certainly does not have the meteorological background to do this. The point being made is that meteorological science does not preclude the building up of chemical energy in weathered material. Rather, there are already such energy-storing processes extant - notably the growth of vegetation and animal growth. Such energy processes are apparently not considered by meteorologists in their calculations, but definitely play a part.

To anticipate later conclusions somewhat, it is suggested that, while the direct effect of solar energy is confined to a matter of feet below the earth's surface, indirectly, through the medium of chemical energy, it may reach deep into the lithosphere. In this there is a certain analogy with the problem of the solar engine, in which some physico-chemical device is necessary for the effective utilization of the solar heat. Geological examples of such energy storing are provided by glaciation, and by coal formation.

Papers dealing with the overall heat economy of the earth are those of Simpson (97) and Geiger (31). Neither author mentions specifically the effect of biological and chemical action on the heat economy, though Geiger does emphasize the variation of the nature of the heat exchange with vegetation, soil and the like.

The magnitude of such effects is quite uncertain, in the same sense that the overall effect on climate of man's presence on earth, and his technological developments, is uncertain.

One final point is that it is not necessary for an excess solar energy to exist over long periods. Thus such a process as tree growth may occur with the earth experiencing a net loss of energy over the period of a day, but receiving energy over a few hours, say. The fundamental reason behind this possibility is the rate effect of physico-chemical transitions, as will be outlined.

If the earth has indeed received a net amount of energy from the sun, conservation of energy requirements indicate that this net energy must be to-day represented by the chemical energy in rocks of the lithosphere. See also page 61 .

Knowledge of the character and amount of the rock in the lithosphere, coupled with closer knowledge of the chemical factor, could provide the basis for calculations of the energy economy throughout geologic history. Such calculations are of course premature in the present state of affairs. In a similar category is the question of the contribution of endothermic weathering reactions to world-wide climatic variations. Should this factor be shown to be important, it is to be noted that the apparently aperiodic character of these changes - that is, referring to glaciation - is easily accommodated by the chemical hypothesis. It would, in fact, be the expected character. The usual hypotheses of the origin of glaciation - with the exception of variation in solar radiation - have difficulty in explaining the above aperiodicity.

An extensive qualitative discussion could be given on this point, but again, such a course would be extremely premature.

Frictional Heat

Frictional heat is not, of course, a primary source. However, frictional processes may localize heat, while the primary energy being dissipated in friction may be completely incapable of such localization per se.

Frictional processes - as involved in rock flowage, or fracture, may be operative in all three of the earth zones described. At the surface, and in the lithosphere, there is good evidence that frictional heat is not an important geologic factor, and there is even difficulty in showing that it has any geologic effects. However, THAT it must have some effect, ~~that~~ is undeniable. In the infra-crustal zone, less can be said of the frictional effect. This may take the form of frictional effects in convection currents, or in mechanical forces due to earth contraction or to attraction of heavenly bodies.

Pekeris (80) has calculated the magnitude of the heat which would be developed by internal friction during convection in the mantle, with the result that it is shown to be negligible relative to the observed terrestrial heat flow. For other models of convection, the precise figures would vary, but frictional heat would probably remain relatively small. De Lury (22) has postulated that frictional effects in the crust are sufficient to develop magmas directly. However, this is an extreme view, and calculations suggest that such frictional effects would be extremely moderate. For example see Nutting (78).

There is abundant evidence of the operation of mechanical forces in the lithosphere, as in shear zones. Even though the direct thermal effect may be small, the deformation obviously has a profound effect on rock minerals. Thus minerals may be strained or crushed, and new minerals may be developed. In this way the mechanical energy may be stored as structural energy, which alters not only the energy content of the region, but also the chemical reactivity. Experimental evidence for these effects is mentioned later in the paper. Geologically, there is abundant field evidence of the reactive nature of mechanically strained material.

c. Geologic environment of the energy sources.

The fundamental characteristics of the infra-crustal, crustal, and surface zones of the earth are sketched below.

1. Infra-crustal. Perhaps the most significant feature of the infra-crustal layers is their tangential homogeneity, as indicated by the reproducibility of seismic velocities. This implies a similar spherical symmetry of temperature, pressure, and composition. The mantle, at least, is essentially solid, and on this basis, the mode of heat transfer most general is probably conduction. On the other hand, there is observational evidence of earthquake foci within the mantle, and slow convection on a broad scale is a very real possibility. In this case, heat transfer by convection would supersede that by conduction, because of the greater efficiency of the latter type of transfer (Pekeris 80). Relative to the upper layers, however, this region is inert and homogeneous.

2. Crustal layers. The crustal layers are characterized by extreme variation in composition, temperature, and stress. Evidence of instability is everywhere apparent. The region is essentially solid, but while conduction is probably the main mode of heat transfer, convection and mass transfer can, and certainly do, predominate locally. The keynote of the region is widespread instability, whose general relief is prevented by the sluggishness of the solid environment, and by continual operation of equilibrium-destroying processes.

3. Earth's surface. This region is characterized by a general high mobility, a consequence of the major role played by the mobile constit-

uent, water, and by the mobility of the omnipresent atmosphere. This makes possible the rapid attainment of equilibrium, which is opposed by the terrific diurnal variation in energy received by the surface, and by the disruption of atmospheric patterns by physiographic variations. The result is the complex nature of weather changes, and the vast difference in local types and products of erosion.

The above is not meant to comprise a complete characterization of the earth zones mentioned. This is the substance of elementary geology, and wouldbe superfluous here. What is intended, however, is a pointing-up of the fundamental differences between the areas involved, particularly as regards homogeneity and mobility of environment. The purpose is to show that a heat source important in one environment may be completely insignificant in another.

d. Importance of Heat Sources in Relation to Geologic Environment.

From the above, it should be clear that the relative importance of the different sources is quite different, depending on which geologic region we are considering.

Primary flow is probably quite ineffective in explaining features of the lithosphere or surface, but may be all-important in deciding events in the deeper zones.

Radioactivity is insignificant at the surface, and possibly of only subsidiary importance, directly, to the lithosphere. However, because of the extreme bulk of the mantle, its highly insulated character, and the possible lack of competing sources, radioactivity may be the prime agent there.

Chemical energy probably has some effect in each zone, but as will be seen, the nature of the effect is intimately connected with the nature of the stability of each zone.

Solar radiation is all important at the surface, but has at present no direct relation to the temperatures in the other zones.

Frictional heat is probably ineffective in the upper zones, but may be important in the mantle.

It is with the above points in mind that the table of page 3. has been made up.

The above points are obvious from a very elementary study of geology, but it is precisely the geological factor that has been most neglected in discussion of the problem.

e. General Natures of the Sources

This paper will be occupied with the effect of chemical energy in geology, but before proceeding to more detailed consideration of this factor, some general relations of the sources of energy should be clear.

Thus primary heat is essentially a ponderous source of great inertia (assuming its existence, of course). There is no possibility of concentrating this heat, at different times and places, intrinsic in the source. Such may be obtained, though, by external disturbances, as deep fracturing, surface aberrations causing convection, and also by storing energy chemically. If such phenomena as ionic diffusion, do occur, local focussing by surface variations in composition seems, qualitatively, to be impossible. (This refers to features of the scale of ordinary rock masses.) In toto, primary heat of itself does not have the characteristics of the source operative in the crust.

The localization of heat from radioactivity seated in the mantle is up against the same obstacles as is the above, unless some unexplained localization of the radioactivity itself occurs. In the crust, there is definite concentration of radioactivity in weathering, and the nature of this is known. Against the localization of radioactive heat in time is the apparently immutable law of radioactive decay. However, as mentioned above, this energy may be entrapped physically or chemically, in which case the problem partly reduces to that of a chemical source.

Cosmic radiation itself admits of no localization, except a very broad latitude effect. Indirectly, the effects of cosmic radiation may vary greatly with difference in local composition of the crust. Again the problem tends to reduce to the chemical one.

Chemical energy, as mentioned, does have the property of possible local concentration. This is true also of localization in time, since the rates of chemical reactions are notoriously dependent on external conditions, particularly temperature.

Frictional energy can be, and usually is, localized. However, because of its nature, frictional energy cannot be increased without increasing the causative energy. In other words, there is no possibility of storing frictional energy as such. Indirectly, there is the possibility of storing such energy chemically. Indeed, much of the surface and strain energy gained by sediments in weathering might be thus classed as due to friction, though the ultimate source is solar.

From the above, it is seen that, besides having the qualities which a petrologically important source should have - ability to concentrate heat in space and time - chemical energy may be related to each of the other source types as an intermediate stage in energy release.

II. CHEMICAL ENERGY AND RELATED PRINCIPLES

a. Chemical Energy

"Chemical" as used in this paper is meant to include such transformations as re-crystallization and phase changes. These might be considered as physical changes, but since the mechanisms involved are precisely those of classical chemical changes, there is little justification for a distinction. A definition of chemical as it is used here might be that it is that energy of a region due to the position of its constituent particles relative to one another. On this basis, radioactivity would probably be included. However, since radioactivity has been so long established as a geologic energy source, it will be kept separate from chemical energy to avoid confusion.

(Radioactivity is the result of the same type of process generally considered to be chemical, the only difference being the nature of the particles involved in the process of equilibrium attainment, and the activation energy per particle required for the process. The magnitude of this activation energy makes the process inert to stimulation by ordinary agencies, as heat, pressure.)

Chemical energy is to-day the foundation of our technology, and examples of it are continually before us. Most important of these are the combustion of coal and oil, but they range from the quiet production of electricity by voltaic cells to the spectacular energy releases of explosions. Perhaps more important are the energies involved in digestion of food.

Aside from technology, natural phenomena offer abundant evidences of the importance of chemical energy. Reactions and transitions involving water, in particular, are behind many familiar weather phenomena. Surface reactions on plants and soils deal in massive quantities of energy, and are fundamental to life as we know it.

The above examples are useful in indicating the ubiquity of the chemical factor, but they are not particularly illuminating as regards geologic reactions. However, situations analogous to the geologic ones, in that the environment is largely solid, occur in a number of cases. For example, in ceramics and metallurgy the role of solid state reactions is well known and appreciated, particularly in sintering. The energy factors involved are receiving increasing attention.

The setting of concrete affords another instance of the chemical effect. In this case, heat is evolved in setting which, in large structures, can lead to destructive fracturing if not taken into account. There is a large number of articles on this point in the literature on concrete.(85).

Spontaneous combustion processes occurring in solids of low conductivity offer more spectacular examples of the energy effect. A large class of explosives has an identical mechanism. Geologically, spontaneous combustion is known in coal, in its natural environment as well as in above-ground storage (60). Similar heating has occurred in sulfide ores stored in mines.

Having given examples of the efficacy of chemical energy, pertinent features of its production and nature will be taken up.

b. Chemical Reaction as a tendency to Equilibrium

The obvious fundamental reason for any transformation is the dis-equilibrium of the system. This is a corollary of the definition of equilibrium, that a system is in equilibrium if it has no tendency to change.. The presence or absence of catalytic agents may be the occasion of a change occurring at a measurably rate, but the direction of the change, and the tendency itself, is entirely due to the nature of the equilibrium obtaining.

It is for this reason that a study of equilibrium and stability is a necessary preliminary to intelligent consideration of chemical reaction. In the following section, some chemical principles underlying equilibrium and reaction rate are discussed.

The source of the energy concerned is to be sought on a molecular scale. Changes in type, length, or number of bonds between atoms all give rise to changes in energy that is ultimately electrical in nature. Such changes may arise from compound formation, mechanical disruption of structure, change of state, or the like. The effect is the same.

c. Stability and Equilibrium

1. Concepts. The distinction between stability in the thermodynamic sense and stability as commonly used is an important one. The following quotation from Lewis and Randall (64) illustrates the main point.

> "In common usage, a system is said to be stable when it undergoes no apparent changes. Now a system which is apparently in a stationary state may be so because it has reached one of the states of equilibrium from which it has no tendency to depart, no matter how great its mobility; or it may be because processes occurring within it are so slow as to be imperceptible, even though the system may be far from a

true state of equilibrium. It is only systems of the first kind which are really in a state of equilibrium which we shall call stable in any thermodynamic sense. Systems of the second kind may be called inert or unreactive."

In principle, this is straightforward enough, but there are practical difficulties. This has led to such concepts as partial equilibrium, false equilibrium, degrees of stability, and "passive resistances to change", the nature of which is sketched below.

Gibbs (32) distinguishes between stationary or equilibrium states due to the balance of the "active tendencies" of the system, and those due to the presence of a "passive resistance preventing change." Passive resistances merely retarding change, of the nature of viscous forces, are dismissed as not entering into the equilibrium. These passive resistances preventing change are considered to be the forces allowing the co-existence of allotropic forms of certain substances. Under Gibbs's scheme, there arises the possibility of reactions which proceed at finite velocity above a certain temperature, and cease completely below that temperature.

Lewis condemns this concept of passive resistance, on the grounds that it is contradicted by the most reliable experimental evidence. Nevertheless, Lewis himself refers to degrees of stability, suggesting that systems may be in equilibrium with respect to small variations in external conditions, but unstable with respect to large ones. As an example of such a system, he cites water at a few degrees below the freezing point. This concept is, however, precisely that of Gibbs (32, p. 59), although Lewis does add that there is a theoretical doubt as to whether any state other than the most stable state is in equilibrium with respect to every conceivable process.

Lewis also introduces the idea of partial equilibrium—equilibrium with respect to rapid processes which may occur within a body, but not with respect to slower ones. An example of this is the case of hydrogen and oxygen dissolved in water being in equilibrium with respect to solubility, but not with respect to the slow water-forming reaction.

In the writer's opinion, there is no theoretical basis for distinguishing between the above-mentioned types of equilibrium. The differences are felt to be a matter of degree only, and due to the fundamental relation between "practical" equilibrium and reaction rate. This view is also supported by the theory of absolute reaction rates.

It will thus be assumed that every process which can lead to a state of equilibrium actually does occur, though perhaps immeasurable slowly. This is also the view of Lewis, despite his discussion of degrees of stability.

Another basic point which should be clear from the above is that a system may be in equilibrium (stable or inert) with respect to one set of conditions, and not with respect to another set. Evidences of this fact are everywhere present.

2. Thermodynamic Dictum of Stability

The thermodynamic criteria for stability of systems are derived in a large number of elementary texts on physical chemistry. These criteria are thus only summarized here. Before doing so, it is well to emphasize the limitations of the various analytic ways of approaching the question of equilibrium - that is, thermodynamics, statistical mechanics, and the kinetic method.

Most important, thermodynamics and statistical mechanics are able to give quantitative predictions only with regard to systems in thermal equilibrium. In particular, they say nothing about the rate of attainment of equilibrium. They ~~they~~ are thus able to predict which is the most stable aspect of the system under any particular set of conditions, but not whether this aspect actually will appear, as the rate of the process involved may be prohibitively slow. The kinetic method is not so limited, but it is far more difficult to apply, and of much less generality. With regard to thermodynamics and statistical mechanics, the latter is much better able to deal with problems of geologic complexity than is thermodynamics. Thermodynamics is able to derive useful relations in terms of the equation of state of the system in question, but is quite unable to derive this equation of state. It depends for this on experimental work.

In the following, P refers to the pressure, V to the volume, T to the temperature, S to the entropy, and E to the energy of the system in question.

The following additional functions are then defined:

F = Free Energy (Gibbs free energy) = $E + PV - TS = H - TS$

A = Work content (Helmholtz free energy) = $E - TS$

H = Enthalpy = $E + PV$

Then for any spontaneous process, it is so that:

$dF < 0$ when P, T are constant.

$dA < 0$ when V, T are constant

$dH < 0$ when P, S are constant

$dE < 0$ When V, S are constant.

Since most processes occur at constant pressure and temperature, the relation involving F is the most important of the above. For a reversible process,

$$\Delta F = \Delta H - \Delta(TS)$$

$$= \Delta H - T\Delta S \qquad \text{, for T constant.}$$

Thus for a process to occur spontaneously at constant pressure and temperature, it is necessary and sufficient that:

$$\Delta F = \Delta H - T\Delta S \qquad \text{be negative.}$$

For this same process, it is obviously so that

$$\Delta H = \Delta F + T\Delta S$$

Then, if the transformation involves a decrease in entropy, $T\Delta S$ is negative, and therefore ΔH , being the sum of two negative quantities, is negative. However, the interpretation of a negative value for ΔH is that the process is exothermic. This result is of considerable importance, since it is frequently possible to predict the general sign or order of magnitude of ΔS . For many solid-state transformations, ΔS is negative - an example is the devitrification of glass - or zero, and solid state reactions which are spontaneous are characteristically exothermic. This point has been discussed more completely by Tammann (93a). Even in those cases where ΔS is positive, ΔH may of course still be negative, depending on the magnitude of ΔF. See page 58 .

Where solid solutions can form, and in other cases where there is the possibility of positive ΔS , an endothermic solid state reaction may still be spontaneous, provided the reaction is not strongly endothermic. See for example, page 78 , concerning calcite and aragonite.

For open systems, the possibility of removal of mass has a complicating effect. An instance of this effect is given on page . Also, varying the temperature and pressure alters F, and may halt or reverse the reaction tendency. The net effect of mass removal, and temperature and pressure variation is given, for a reversible process, by Gibbs (32, p. 87):

$$d\Delta F = -\Delta S\, dT + \Delta V\, dp + \sum \mu_i\, dn_i$$

Where μ_i is the chemical potential of substance i, and n_i is the number of modes of that substance.

When ΔF is small, it is obvious from the above equation that alterations in temperature and pressure caused by the reaction itself may alter ΔF considerably. For substances far from equilibrium, which situation is of most interest in this paper, the effect is less important. In any particular case, the actual effect could be estimated from heat data.

d. Kinetics of Reactions

1. General Principles. Perhaps the most distinctive feature of the theory of the kinetics of chemical change has been its inability to predict the rates of individual reactions with any degree of success. This situation has been changed somewhat in the last few decades, with the development of the so-called "theory of absolute reaction rates." Nevertheless, the general theory is still incomplete, and the bulk of current research is occupied with explaining variations in observed rates from "classical" values. The complexity of the factors which may influence reactions is even more apparent in reactions in and

between solids, than in gas or liquid reactions. The special features of solid state reactions are discussed later.

Despite the shortcomings of the theory, there are some generally accepted facts, or perhaps usages. Thus for the reactions $A + B + C = \text{products}$, the rate of disappearance of the reactant A can be expressed by

$$\frac{d(A)}{dt} = -k\,(A)^{a}(B)^{b}(C)^{c} \tag{1}$$

Where (A), (B), (C) are concentrations, and $k = f(T)$ alone. The coefficients a, b, c are experimentally determined, and are in general not integral. In this expression (1), the sum $(a + b + c)$ is called the "order" of the reaction, and k the specific reaction rate. Also, a is the order of the reaction with respect to A, etc.

It is commonly agreed that the specific reaction rate k is of the form:

$$k = C e^{-\frac{q}{RT}} \tag{2}$$

where T is the temperature, and C, q are constants, provided the range of T is not too great.

In this equation (2), C is called the "collision frequency", or "frequency factor," and q is the "activation energy". Both may be considered constant for purposes of this resume, and are experimentally determined from the temperature dependence of the reaction rate. Physically, q may be thought of as proportional to the minimum excess energy which the reactant molecule-complex must possess if it is to decompose into the products. The intermediate molecular state is called the "activated complex", and is assumed to have the ordinary properties of a molecule, with the exception that slight disturbance can lead to its dissociation. In unimolecular reactions, this complex will not differ much from the molecule itself, while in bimolecular and termolecular reaction, it may be an unusual configuration born of collision. The name "collision frequency" is due to the relation which this factor has to the collision frequency of molecules in gas- and liquid-phase reactions.

The form (2) is due to S. Arrhenius (in 1889), and has been the stimulus for most of the subsequent work on kinetics. It should be noted that it is of such a form that small changes in q result in large changes in k. Such variation in activation is the explanation of the frequently-great differences in rate, and particularly in temperature-dependence of rate, between reactions that are formally similar.

With the picture given above of the physical meaning of q, it is plain that if the structure of the reactant molecule - considering a unimolecular transition for simplicity - is very different from that of the product, q will tend to be large, as the reactant must then be strongly distorted before it can pass over freely to the product. Mineralogically, it is the variation in activation energy which accounts for the sluggishness of "reconstructive" transformations relative to "displacive" ones.

It is to be noted that the form of (2) occurs also in the theories of diffusion of viscosity, and of radioactivity - wherever a process depends on a particle surmounting a local potential barrier ~~before reaching another - perhaps also temporary potential barrier~~ before reaching another - perhaps also temporary - equilibrium position.

The concept of the activated complex is more clearly outlined in discussions of the theory of absolute reaction rates. The most comprehensive study is that of Glasstone, Laidler and Eyring (35). Several briefer presentations are given in Smoluchowski's symposium (102).

The parameter **C** depends greatly on a number of factors which are difficult to take into account rigorously. That is, it is related to the entropy change in the formation of the activated complex, and thus withthe structure of the complex, and with the environment in general.

Finally, every reaction may be thought of as consisting of a number of steps, in which each step has associated with it a different rate. In many reactions, one step is so much slower than the others, that this step is effectively rate-determining. However, in others, this simplifying factor is not present, and the net rate is a complicated function of the individual rates.

2. Solid state reactions. Until fairly recently, it was no exaggeration to say that chemical thought on solid state reactions revolved largely around the ancient dictum: "corpora non agunt nisi fluida", a view which persists in some quarters even today. However, great strides have been made in this field on both the experimental and theoretical side, and there is now a large body of literature on the subject.

The history of work on the subject covers a rather brief period. At the end of the last century, diffusibility of metals and carbon was discussed by Roberts-Austen and others. Work on metallography continued at the beginning of the century, but it was not until 1910 that the first real investigation of a solid state reaction between non-metallic reactants was made (16). This was an additive reactions between oxides to form solid solutions, and it was found that the reactions depended greatly on particle size, and previous treatment of the material.

The chief evidence, aside from direct observation, that such reactions are solid state reactions, and do not occur via some sort of gaseous phase, is the connection of the reactions with factors which are evidently characteristic of the solid state. Solid-state reactions are structure-sensitive to an extreme: experiments have shown conclusively that every interference with the crystal lattice which sufficiently decreases the internal stability increases the ionic mobility, and hence stimulates the reaction. Factors which weaken the structure are: heat, changes in symmetry, presence of impurities, and various lattice defects. When a crystal is experiencing a polymorphic change of form, it is particularly reactive. This is especially so for reconstructive changes, which is not surprising, because such involve at least temporary breaking or weakening of many of the atomic bonds.

The extent to which impurities may influence reactivity is shown by the reaction

$$BaO + PbCl_2 \rightarrow BaCl_2 + PbO$$

as cited by Hedvall (42C). For this reaction, the addition of 0.10 molar percent of $BaCl_2$ as solid solution in the $PbCl_2$ increased the amount of reaction almost 100% at some temperatures. The effect is most noticeable at lower temperatures.

Another instance of this sort is provided by the reaction

$$Fe_2O_3 + CaO \rightarrow CaO \cdot Fe_2O_3$$

studied by Hedvall and Sandberg (43). These investigators prepared the Fe_2O_3 used in two different ways, one of which produced crystals of high surface and strain energy. The higher energy reactant had a striking effect on reactivity, with a 100% increase in yield locally. This effect was, again, greater at the lower temperatures.

Perhaps the most significant feature of solid-state reactions is that the rates are generally diffusion-controlled, in that diffusion rate is much slower than the rate of actual formation of chemical bonding once the atoms are contiguous. Certainly if there is no possibility of diffusion there can be no reaction. This dependence of reaction rate is on the anion rather than the cation of the crystal structure. To illustrate this, the reactions of BaO, SrO, and CaO with $MgSiO_3$ gave initiation temperatures (the temperature at which the first rapid rise of reaction rate is noticed) of 355, 453, and 562 degrees Centigrade. The initiation temperatures when other silicates — wollastonite, sillimanite, rhodonite — were substituted for enstatite were almost identical. Now the anions — in this case oxygen ions — control the bulk aspects of the silicate structure, and the above result is not anomalous, since diffusion through similar structures is the controlling factor in each case.

As far as the extent to which solid state reactions occur in geology is concerned, the general solidity of the reactive medium cannot be doubted, for most metamorphic processes. There are too many examples of preservation of delicate structure in replacement, and similar evidence, to dispute this. It is then so that, if the reactions involved are, as in some cases, contemporaneous, each individual reaction must have been largely solid state.

On the other hand, it is certainly so that there are sufficient pore fluids present in most geologic situations for fluids to abet the reactions, and in other reactions, water is a product. The actual case is some combination of both effects. It is probably of doubtful significance to distinguish betweeen them in the geologic case: there is surely every gradation between a compressed, impure liquid adsorbed on mineral grains, and the "solid" dispersed phase at grains boundaries or reaction fronts.

The most complete works on solid state reactions are those of Hedvall (42A) and Jost (52). ~~The most complete works on solid state reactions are~~ The most recent review of solid state reactions in English, of which the writer is aware, is that of Cohn (18). This is a thorough summary with an excellent bibliography. A bibliography of Hedvall's work, complete to 1950, is given in references (42D). Geological discussions have been given by Taylor (111), Perrin (82), and Bugge (13). A reference in which topochemical effects are emphasized is that of Cohn (17).

3. Thermal autocatalysis. That process, in which a reaction alters the temperature of its environment, and hence the velocity of subsequent reaction, may be termed thermal autocatalysis. This condition may arise for either endothermic or exothermic reactions, but it is obvious that only in the case of exothermic reactions is there the possibility of an increasing rate of change of temperature.

Instances of this exothermic autocatalysis are very familiar, and often very spectacular. This is the case in many explosive reactions, for which class of reaction the thermal mechanism is very common. Spontaneous combustion reactions, generally, are of this type.

Fundamentally, thermal autocatalysis must arise in any case where the rate of establishment of thermal equilibrium is less than the rate of heat production or absorption by the reaction. On this basis, the effect is probably of wider occurrence than is usually recognized. In non-violent instances, it would be difficult to detect simply. On a molecular scale, there is a certain analogy with the necessity of a third body in some bimolecular syntheses, for the purpose of carrying away part of the energy of the reaction.

Thermal explosions in gases must be initiated suddenly, as a result of a strong local stimulus towards reaction: e.g. a spark. This is because of the relatively high efficiency of heat transfer in gases.

In material in which heat flow is less efficient, such as in certain solids, reactions are able to begin catalysis with much less sharp stimuli. For the same reason, reactions in such material may show much longer induction periods. Examples of long induction periods of this sort are common in cases of spontaneous combustion - such material as coal or oily rags may smoulder for many months before igniting.

The significance which such topics have for geology is due to the very low conductivity of rock material, and the correspondingly low rates of geologic reactions. At constant temperature, many geologic reactions are extremely slow, but in those cases where the reactions are exothermic, the possibility of thermal catalysis must always be considered as an accelerating device. Such thermal catalysis is particularly striking in the case of slow reactions, because such reactions usually have a large activation energy, and hence very great temperature-dependence for their rates. This is apparent from equation (2) above.

The mathematics of thermal autocatalysis will be indicated in a later section, along with estimates of its likelihood in geology.

e. The role of reaction rate in physical processes.

The role of rate of reaction in deciding just which phases will occur is so important and interesting, that a further discussion of it is warranted.

As familiar examples of the utilization of the effect of reaction rate in industry, we have the cases of steels and glasses. Here rapid cooling forestalls attainment of thermodynamic equilibrium. Again, in the Birkland-Eyde process for NO production, the crux of the process is the rapid cooling of the NO from the arc temperature. At ordinary temperature, NO is not stable, but its rate of decomposition is extremely slow.

If sufficiently rapid heat removal is achieved, water will freeze to ice, despite the fact that the vapour may be the stable phase. A second process of sublimation will then follow. This phenomenon is very familiar in northern countries in winter. A slower rate of cooling would of course preclude the appearance of the solid.

The chilling of a lava flow presents a somewhat analogous situation, in which the balance is between the rate of crystallization and rate of cooling.

Rate effects are also important on a molecular scale. Many, if not most reactions occur in steps, and the total observed rate is due to the combination of the separate rates. This is one reason for the difficulty of predicting rates, since the reaction mechanism is often extremely dubious. Then, also, the separate rates may have different responses to external conditions, which can lead to very confusing results. Frequently, the rate of one step is so much slower than another that it is effectively the rate-determining step. There is therefore the possibility of the local attainment of partial equilibria, and the formation of temporary stages. Evidences of such temporary stages in rocks need not imply, therefore, a complete change of external conditions, or successive waves of metamorphism, but may easily be part of the natural order of things. The present existence of such minerals as wurtzite and cristobalite may be explained on this basis, as being entirely due to the rate effect.

If the thesis that chemical energy is of geologic importance is correct, reaction rate has a very fundamental role indeed. For it is only because of the inadequate rate of attainment of equilibrium relative to rate of mechanical transport, or heat removal, that large rock masses are in disequilibrium.

The effect of step mechanisms in rate may explain certain contact effects. Here rare mineral types may occur near contacts, because reactions proceeded between the products at hand, and broader satisfaction was prohibited by the necessity of longer distance diffusion. In the same vein, it is clear that, while there is no theoretical limit on the validity of assuming the existence of processes tending to equilibrium, the scale of things must be kept in mind. Thus, the broad divisions of the earth as a whole - crust, mantle and core - are probably unstable with respect to some particular melange of the three, but the rate of the process may be negligible even for cosmic times. This broader scale of instability has been discussed by Ramberg (84).

A final indication of the role of reaction rate in earth processes is provided by Lewis (64, p. 566). Thus, from free energy data, Lewis calculated that, starting with water and air, nitric acid should form until a concentration of 0.1 M is attained. This reaction has of course not occurred, even over geologic times.

III. EXPERIMENTAL METHODS

a. Measurement of Transformation Heats

Basic to any discussion of the role of chemical energy in geology is a knowledge of the heat effect associated with reactions known to occur geologically. In this section, some of the methods via which this knowledge may be obtained are described. A more complete discussion is given by Eitel (23).

These Are:

1. Direct measurement
2. Cyclic processes
3. Cohesive energy calculations
4. Thermodynamical relations

1. Direct Measurement

The most straightforward method of obtaining the required values is, of course, direct measurement on the transoformation in question. However, it is obvious that not all reactions of geological interest are amenable to such an attack. In particular, many silicate reactions are so slow under laboratory conditions that no significant values could be obtained thus, and many other reactions cannot be reproduced at all. Nevertheless, there are reactions to which the method can be applied at ordinary temperatures, and others can be investigated using somewhat specialized techniques.

Ideally, the reactants are introducted into some sort of calorimeter, and, taking mechanical heat losses into account, the heat of reaction computed from the temperature rise and specific heat of the calorimeter—plus-contents system. Complications arise for slow reactions because heat losses mechanically - i.e. by radiation, convection, etc., may become comparable to the reaction heat. The lack of certainty regarding such heat losses then increases the error.

Reactions which require higher temperatures for their propagation to occur in reasonable time may be studied by supplying a known amount of heat to the reactants, again in a calorimeter device. Thus in the combustion calorimeter, a known amount of carbon is added to the reactant mixture and ignited, the adiabatic rise in temperature ensuing from this reaction serving to accelerate the reaction. To obtain the desired heat of reaction, the heat developed when the carbon alone is burned is measured, and subtracted from the heat developed by carbon plus the reactants. This was the method used by Le Chatelier (50) in his peoneer work on the silicates, in 1895. It has been described by Mellor and Holdcroft (71). Aside from the usual error of radiation loss, the chief drawback of this method is lack of control over the state of the products. That is, the desired reaction may not go to completion, and complicated side reactions may occur. It is then frequently the case that the measurement is so tied up with poorly known quantities as to be of little quantitative use.

Other methods of supplying the requisite initial temperature employ electric heating elements, or preheating. With due regard to energy input, hydrothermal reactions could conceivably be studied, but the results would again be dependent on a number of subsidiary heat values, errors in which might be additive. Also, attempts at controlling conditions of reaction, while at the same time keeping account of the energy balance, would lead to rather complicated devices.

Differential methods achieve a notable improvement, in that, by balancing out extraneous effects, the significant quantity is measured directly. There are many different forms of such differential devices, and modifications can be made to suit individual cases. It is therefore impractical to describe any particular type. The general principles of heat of reaction measurements using a differential instrument of the dynamic type are given by Wittels (124).

Despite its well-known advantages as a qualitative tool, the method suffers in quantitative application because of the following: lack of control over reactions occurring, impossibility of dealing with sluggish reactions, and the effect of overlapping reactions. The usual instruments are also handicapped by small charge capacity, with consequent sensitivity to small extraneous variations. Some of these disadvantages might be overcome in specialized devices, and the method is therefore of importance.

To summarize, the chief drawback of direct measurement is the general difficulty of considering a unique reaction.

2. Cyclic processes

Since the heat effect attending transformations can be expressed in terms of the heat contents of the reactants and the products, and the heat content is a state function, it follows that the heat of the transformation is independent of the manner in which the transformation takes place. This is the usual statement of "Hess's" law". The same concept is embodied in the utilization of so-called cyclic processes. Thus from the properties of state functions, the net change in any state function resulting from any cyclic process whatever, is zero.

The most common use of cyclic processes as regards reaction heat is in determining the heat of reaction at various temperatures from measurement of the specific heats of the substances involved, and the heat of reaction at any one temperature. The cycle is:

$$\begin{tikzcd}
\underset{\text{REACTANTS}}{T_1} \arrow[r, "A", "(\Delta H_A)"'] & \underset{\text{PRODUCTS}}{T_1} \arrow[d, "B", "(\Delta H_B)"'] \\
\underset{T_2}{\text{REACTANTS}} \arrow[u, "D"', "(\Delta H_D)"] & \underset{T_2}{\text{PRODUCTS}} \arrow[l, "(\Delta H_C)"', "C"]
\end{tikzcd}$$

For which

$$\begin{aligned}
\Sigma \Delta H = 0 &= \Delta H_A + \Delta H_B + \Delta H_C + \Delta H_D \\
&= \Delta H_A + \Delta H_C + \int_{T_1}^{T_2} \frac{dH}{dT} dT + \int_{T_2}^{T_1} \frac{dH}{dT} dT \\
&= \Delta H_A + \Delta H_C + \int_{T_1}^{T_2} C^P dT + \int_{T_2}^{T_1} C^R dT \quad \text{——} \quad (1)
\end{aligned}$$

Where C^P, C^R are the heat capacities of the products and of the reactants, respectively.

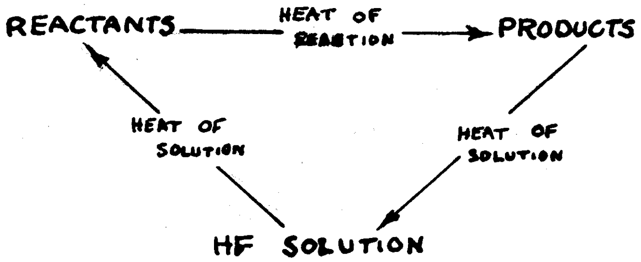
At constant pressure, $-\Delta H$ is the heat evolved in the reaction, and C^P, C^R become C_p^P, C_p^R, the heat capacities at constant pressure.

Such usage is of the utmost practical importance: values for reactions which proceed only above a certain temperature, or which can be made to occur only under certain unique conditions, can be obtained for any set of conditions, provided that the necessary specific heats, compressibilities, and such are available.

Use of the cyclic principle is thus made in every sort of heat of reaction determination in some way. However, a more direct use is in determining heats of reaction from differences in heats of solution, or of fusion, and from cohesive energy calculations. These cycles are discussed below.

(i) Heat of solution method.

The simplified cycle is:



The method depends on the existence of a solvent capable of dissolving the substances involved with reasonable rapidity. For silicates, hydrofluoric acid is employed, alone or with minor additions of other acids. Errors arise chiefly because, even in the case of the most soluble silicates, the solution process is slow, and certain other silicates are practically insoluble.

Determining heats of formation of silicates from their heats of solution in HF seems to have been first attempted by Cunningham (20). His experiments were semi-quantitative only.

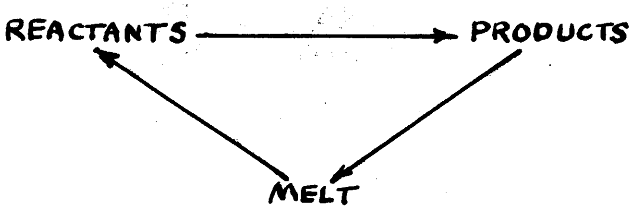
Tammann (107) discussed the basis of the method, showing that the end products of solution of quartz glass and quartz crystals in HF were the same.

The first extensive work was that of Mulert (75). His results and general method are discussed later. Later work has led to general improvement in the instruments used, but no essential changes in method. (An exception to this is the work of Ray, (86). Mulert's method was to measure the temperature rise caused by complete solution of a known amount of substance. The achievement of complete solution in reasonable time was possible only with very finely-powdered materials. Such material obviously does not have the same energy content as the un-ground macro-crystal. This point is discussed on page 66 . Ray circumvented this difficulty to some extent by using an excess of solute, and quenching the reaction with cold water. In this manner it was possible to use coarser material, and achieve much larger temperature rises in the solutions.

The advantage of the heat of solution method is that it permits the investigation of a large number of specific reactions with the same equipment, and with complete control over the nature and state of the products. (However, reactions at high temperatures, and pressures can be considered only indirectly).

(ii) Heat of fusion method.

Here the cycle is



This method is similar in principle to the heat of solution method, but is, theoretically at least, of universal applicability. In the case of refractory materials, the heat of reaction may be small in relation to the total mechanical heat of the samples, in which case the desired result appears as the difference between two large numbers. This is also true of the heat of solution method.

The writer is not aware of any data obtained by this method, but it would seem to be well worth investigating, particularly since it affords the possibility of directly studying reactions at high temperatures and pressures.

3. Thermodynamic relations

There are many thermodynamical expressions which relate physically observable phenomena to the fundamental thermodynamic functions F, H, E, ... In some cases, such relations may be used to obtain values of these functions. The general concept will be clear from the following example.

Thus, for any reversible transformation, there is the Van't Hoff relation $\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2}$, where K is the equilibrium constant for the reaction.

This makes possible the determination of ΔH from data on the change of equilibrium constant with temperature. For examples of this usage see Lewis (64) page 298.

Again, the familiar Clapeyron relation, one form of which is

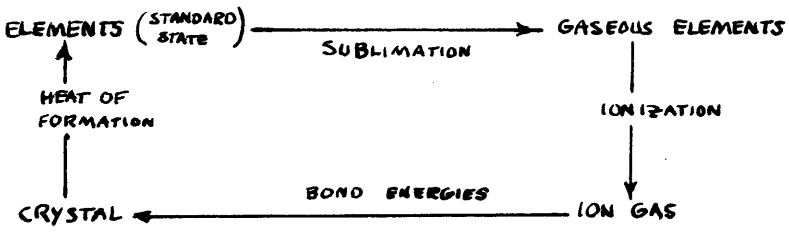
$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H}$$

can give ΔH from observations on the change of transition temperature with pressure, and the volume change. This relation has been used directly by Bridgman (8) to determine heats of transition. Indirectly, the Clapeyron equation can be used to derive a relation between the freezing point of a solid solution and its composition, which expression again includes ΔH. This relation is derived by Lewis (64), page 238. It has been frequently used to calculate latent heats from date given on silicate phase diagrams. An example of this usage is given by Bowen (8).

There are a number of other relations of a similar sort, mostly of less general applicability. Many of these thermodynamic relations are rendered less valuable because they apply strictly only to ideal systems. This difficulty is discussed by Bowen (8).

4. Cohesive energy calculations

Calculation of cohesive energy or structure energy (sometimes erroneously called lattice energy) involves using a cycle of the following sort:



The above cycle is frequently called the Born-Haber cycle.

Existing calculations deal with simple substances only, as the alkali halides, monovalent metals, and certain rare gas solids. Thus metals, ionic crystals, and molecular crystals have received some quantitative treatment. Unfortunately for the study of silicates, there have been no complete energy calculations for valence crystals. Since silicate bonding may be considered as partly ionic and partly hemopolar, calculations based upon ionic bonding alone leave much to be desired. Such calculations have been made by Hylleraas (44).

Calculations which would take into account the homopolar effect are not intrinsically impossible, but for even the simplest homopolar crystals, so many valence electrons are affected by the binding that the calculations are extremely complicated. A semi-quantitative treatment of the bonding in diamond has been given by Kimball (58).

Cohesive energy calculations are at present of little practical use for the determination of heats of reaction. Even for the types of bonds amenable to calculation, agreement of calculated with measured values is only fair. This is partly because real crystals contain many minute flaws which are impossible to describe mathematically. Approximations can be made, but the main purpose of calculations in the present stage of knowledge is to check the theory, rather than supplement measurement.

An excellent resume of work on cohesive energy is given by Seitz (94) Chapter 12.

b. Reaction rate determination

Methods of determining reaction rates depend very much upon the type of reaction to be studied. However, a concept which is employed in all determinations is that of "measure". This is defined as follows:

$$y = \frac{M_0 - M_t}{M_0 - M_\infty}$$

Where y is the fraction of material reacted, M_0 is the measure at time $t=0$, M_t the measure at time $t=t$, and M_∞ the measure at time $t \to \infty$.

In the most simple case, the measure used will be the amount of reactant or product directly. Otherwise, the measure may be the pressure of the system, the density, or any physically measurable property which alters as a result of the reaction, and which bears an approximately linear relation to the reacted mass. Some of the measures used are: electrical conductivity, thermal conductivity, magnetic susceptibility, and optical properties. Choice of the measure to be used depends on various factors, such as the accuracy with which the measure may be determined, its uniqueness in regard to the reaction which is to be studied, and its range of variation during the reaction.

As a simple example of use of pressure as a measure, consider the gas decomposition into gaseous products according to $A \rightarrow 3B$. Assuming perfect gases the pressure after a long time would be $P_\infty = 3P_0$

where P_0 is the initial pressure. Then if the pressure at time t is P, we may follow the progress of the reaction using:

$$\text{FRACTION REACTED} = \frac{P_0 - P}{P_0 - 3P_0} = \frac{\Delta P}{2P_0}$$

For measures which do not bear a linear relation to the quantity of material reacted, more specialized equations may be constructed.

In studying the rates of solid-state reactions, knowledge of the reaction mechanism, and of the properties of the reactants and the products is essential to intelligent choice of a measure or measures.

Solid-state reactions commonly alter or destroy the original structure, and the reaction therefore alters a number of structure-dependent properties. Such properties can be used as measures. The difficulty is in discovering the relationships between them and the degree of reaction, in the case that these relationships are not linear. It is therefore useful to employ several measures, which may then throw light upon not only the rate of reaction, but also upon the reaction mechanism. The work of Huttig (<u>47</u>) presents examples of the use of measures of solid-state reactions. See also Buerger (<u>11</u>).

For step reactions, it may be possible to study the kinetics of the rate-determining step, if such exists, separately from the main reaction. For a solid-state reaction in which the slow step is the diffusion of the reactants to the reacting interface, the study of the diffusion rate may be made a separate problem. The advantage in separate study is that it is thus simpler to investigate the influence of external agencies, such as electric potential, radiations of various sorts, and the like, on the reaction. Such investigations usually provide information on the reaction mechanism.

The study of extremely fast and extremely slow reactions presents problems that must usually be solved for the individual cases, and it is not feasible to discuss such here.

Calculation of reaction rates from the theory of absolute reaction rates can provide an approximate answer, but exact determinations are not yet possible. The reason for this is partly that the theory is inadequate, and partly that real crystals (in the case of solid-state reactions) depart considerably from ideality. Cox (19a) has used the theory of absolute reaction rates to calculate the rate of devitrification of silicic glass.

In those cases where the geologic evidence for a particular reaction is clear, and the external conditions obtaining during the period of reaction can be estimated, it may be possible to compute reaction rates from a knowledge of age relationships. A specific example of a rough calculation of this sort is given on page 89. More generally, it will be clear from the forthcoming discussion of the mathematics that it is theoretically possible to calculate from geologic observations any of the parameters involved, provided enough is known of the remaining parameters. In practice, it will usually be impossible to obtain reliable data in this way, at least at present.

c. Geologic significance of the measurements

The most important point to be considered when attempting to determine the heats or rates of geologic reactions is whether the laboratory reaction is a sufficiently good approximation to the actual reaction.

This is particularly so with regard to the rate determinations: the most detailed studies on the kinetics of a solid state reaction are quite unable to yield quantitative data on a geologic reaction which takes place *via* pore fluids, for example.

Results of experiments should be judged, not merely on their accuracy relative to the artificial system studied, but on their compatibility with geologic facts. The rock itself is the final arbiter, and we must not allow our enthusiasm for results gleaned from study of artificial systems to blind us to the possibility that the actual geologic system is fundamentally different.

IV CHEMICAL ENERGY AND GEOLOGY

a. Previous Work on Chemical energy in Geology

There is a conspicuous scarcity of previous work on the chemical factor in geology. Where allusion has been made to this energy factor, it has usually been such as to suggest that large quantities of heat are necessary to achieve metamorphism. As concerns some reactions, this may of course be true, but in general the endothermic concept seems to have grown up out of a confusion between heat necessary to raise temperatures to the point where reaction rate is appreciable, and that actually required to make the reactions thermodynamically possible.

The distinction between the two is quite clear in the two definitely exothermic processes of devitrification, and sintering of a monomineralic powder. Thus, to achieve devitrification, or recrystallization, some heating is necessary to increase the rate to a point where there is an appreciable yield. However, all of this heat, and more, is recovered on completion of the process. It is easy to see how such a confusion could arise from field observation - recrystallization and devitrification, for instance, being observedly associated with possible sources of heat, such as dykes, intrusions, fissures.

Another factor seems to have been the predominately magmatic tone of thought prevailing in the Anglo-German school until recently. Thus, many metamorphic processes were visualized as involving fusion as an essential step. The fact that this is a highly endothermic process then may have helped to becloud the issue.

In any case, the tradition has been that mineral changes absorb heat, which dictum has been repeated or implied with small effort to investigate its validity.

Although there has been no unified treatment of the relation of chemical energy to geology, of which the writer is aware, individual aspects of the problem have been considered in varying degrees. In the following sections some of the pertinent references are cited and discussed.

To foster clarity, the papers have been grouped accordingly as they chiefly concern or stem from:

a. Fundamental principles and mechanism

b. Field and laboratory observations

c. Geologic role and implications.

The list is undoubtedly incomplete, at least as concerns papers with only minor allusions to the problem, but will indicate the general scope of previous work. The nature of the more pertinent papers is mentioned below.

a. Fundamental principles and mechanism

1. Surface and strain energy.

(2) Bain, W., The mechanics of metasomatism. (1936)

(11) Buerger, M. J., and Washken, E., Metamorphism of minerals. (1947)

(26) Fairbanks, E.E., The mechanism of replacement and recrystallization (1925).

Verhoogen, J., The geologic significance of surface tension (1948).

2. Reactions

(81) Perrin, R., Le metamorphisme generateur de plissement. (1935)

(82) Perrin, R., Les reactions a l'etat solide et la geologie. (1937).

(83) Perrin, R., and Roubault, M., Le granite et les reactions a l'etat solide (1939).

(10a) Bridgman, P.W., Polymorphic transitions and geologic phenomena (1945)

(84) Ramberg, H., The tehrmodynamics of the earth's crust. (1947)

(13) Bugge, J. The geologic importance of diffusion in the solid state.(1945)

(27) Fenner, C.N., The chemical kinetics of the Katmai eruption.

b. Field and laboratory observations

(27) Fenner, C. N., As above.

(73) Misch, P., Metasomatic granitization of batholithic dimensions.

(66) Lovering, T.S. Geothermal gradient and sulfide oxidation.(1948)

(25) Emmons, W. H., On temperatures in zones of chalcocitization.

(11) Buerger, M.J. and Washken, E. As above.

c. Geologic Role and implications.

(10b) Bridgman, P.W., Polymorphic transitions and geologic phenomena ( )

(81) Perrin, R., Le metamorphisme generateur de plissement (1935) ( )

(25a) Evans, R.D., et al Radioactivity: a the earth's heat and geologic age measurements (1942).

(117) Van orstrand, C.E. Observed temperatures in the earth's crust.

1. Surface and strain energy

The fact that a strained body, or one that has a large specific surface area, represents a high energy form, has long been recognized. Leith discusses the general principles briefly. Fairbanks gives a more complete qualitative explanation of the origin of the excess energy, with suggestions as to geologic applications. Bain provides a similar discussion, and mentions the application of surface tension to ore deposition. Buerger discusses the origin of the energy qualitatively. Verhoogen writes down the classical thermodynamic relations of surface tension, and, citing Bain, suggests that surface tension may have some geologic effect.

None of the papers consider the heat effect which may arise, or estimate the amount of strain or surface energy quantitatively.

2. Reactions

Only two papers were encountered in which thebasic principles underlying the reaction tendency are discussed. Bridgman suggests that changing conditions may lead to deep seated phase changes in the mantle, but is not particularly occupied with the physical reasons for the changes. Ramberg, in his more general discussion of the thermodynamics of the earth's crust, recognizes the fact that, while thermodynamic equilibrium will tend to prevail in any particular locale, it will only be realized where the rate of chemical transport is greater than the rate of mechanical transport. He pictures instability of molecules under chemical and mechanical stress as leading to diffusion over large distances. Mention is not made of the energy factors. Bugge emphasizes the role of diffusion in solid state reaction. Also, in a single sentence, he mentions that solid state reactions might catalyze themselves thermally.

b. Field and laboratory observations

Fenner, from observations of Katmai volcano, concludes that the field facts clearly imply that exothermic reactions are the heating agents operative. Misch suggests, in a sentence, that local exothermic reactions may have aided crystallization in parts of the granitized area of Yunan, China. Buerger and Washken have conducted laboratory experiments on crystal powders to test the efficacy of strain energy. The heat effects are not considered by them. Emmons and Lovering have calculated the heat effects of sulfide oxidation, and Lovering has considered the effect of this oxidation on the near-surface thermal gradient.

c. Geologic role and implications

Bridgeman, already cited, stresses the possible effect which the presence of phase changes would have on theories of crustal structure. Perrin and Roubault, in several discussions of granitization, discuss solid state reactions. However the writer has found no reference to the nature of the energy economy in these works. One exception to this might be Perrin's paper on the relation of metamorphism to folding, in which folding is ascribed to the supposed volume increase in granitization. The example of volume increase which he gives is too naive to be considered seriously for itself, but possibly he has also other, more reasonable, effects in mind.

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Finally, a few references concerning themselves with energy sources within the earth mention the possibility of reactions. The only such ones which this writer has seen are by Van Orstrand and by Evans et al. Van Orstrand considers that chemical effects would be of a minor nature, while Evans states that, although exothermic and endothermic reactions exist within the earth, their "exact and overall importance is quite uncertain."

6. Preliminary Discussion of Chemical Energy in Geology

The preceding sections have included discussions of the general principles underlying instability and reaction rate, together with a few examples of thermal autocatalysis. In this section it is proposed to discuss qualitatively whether chemical energy is likely to be geologically important in the present sense.

First off, aside from the sign of the heat release in the reactions, there is absolutely no doubt that the reactions have occurred, and that there must therefore have been some effect. This must be so at least locally - on a broader scale there is the possibility of an equilibrium being approached, and exothermic reactions being balanced by endothermic ones. Note, however, that such a situation could occur only over a limited temperature range, and for certain specialized conditions. Even then the chances of it occurring seem very remote.

With regard to many important reactions being exothermic, this can be decided after study of the reactions according to the methods of the preceding chapter. Qualitatively, however, there appears to be a philosophic resistance in the geologic literature to the assumption of exothermic metamorphic reactions on a broad scale. It will thus be useful to discuss the problem from this point of view, with the purpose of showing that exothermic reactions are not precluded by broad geologic reasoning.

The following evidences seem to exist.

1. The geophysical need for a heat source in the crust
2. The indicated spontaneity of many geologic reactions
3. The ease with which the exothermic concept is tied in with the terrestrial heat economy as a whole.

These will now be discussed roughly in turn.

1. The geophysical need for a heat source has been discussed in Chapter I. The main features and failings of the principal sources appealed to have been mentioned, with the result that chemical energy has been shown to be at least a minor factor, and quite possibly a major one. Certainly such a source has the correct qualities. This argument of course loses some of its suggestiveness if we are inclined to admit the presence of some as yet unknown source, and thus, perforce, achieve a sort of defeatist immunity.

2. The apparent spontaneity of many metamorphic reactions is very striking. There are very many cases in which porphyroblasts are surrounded by spherically symmetric haloes, without the slightest evidence for solutions having entered via cracks or via volume diffusion, or of there having been "baking". That is, there is in many cases no evidence of a chemical or thermal wake. Even if we say that this is again a mysterious diffusion of which we are as yet ignorant, there is often the positive evidence of the haloes. These suggest that the driving force for each reaction is centered at the crystal itself: that is, that the reactions are spontaneous.

That this situation cannot be shown in more cases is usually due to the presence of other grains which obscure relations, or to the perhaps-fortuitous presence of channelways which provide a basis for doubt. Ideally, the relation is shown by porphyroblasts in homogeneous media composed of minerals sensituve to physical and chemical change, as clays or shale masses.

That spontaneity of solid-state reactions implies that they are exothermic has been indicated by Tammann, and is discussed on page 26. More generally, this is suggested by the relation

$$\Delta F = \Delta H - T\Delta S$$

where ΔF is to negative for a spontaneous reaction. Now by the statistical concept of entropy which considers it as related to the logarithm of the disorder, or randomness of structure, it is obvious that ΔS will in general be negative for upgrade metamorphic reactions. Thus the factor $-T\Delta S$ will be positive, and if the reaction has truly been spontaneous, then ΔH must have been negative and greater in magnitude than $T\Delta S$. As stated on page 26, the criterion for an exothermic process is that ΔH shall be negative.

Even for reactions in which ΔS is positive, $T\Delta S$ is unlikely to approach in magnitude the ΔH term at temperatures below the point of fusion. This is suggested by a comparison of the magnitude latent heats of fusion of silicates with average heats of reaction. The complicating effect of an open system has been mentioned on page 27, and is discussed also below.

In apparent contradiction to the above is the seeming spontaneity of the weathering reactions. These involve, in many cases, the same minerals as do the anamorphic reactions, and it is reasonable to protest that both sets of reaction cannot be spontaneous. To resolve this apparent anomaly, two possible lines of thought may be followed: either both sets of reactions occur spontaneously, and the difference in sense of reaction is due to the variation of the intensive parameters of the system, or the reaction of one environment is not truly spontaneous, external work being done to achieve it.

The significant difference between the weathering environment and that of induration would seem to lie in the nature of the water. In weathering, clay formation is characterized by the presence of water undersaturated with respect tothe metallic ions. Thus in the case of the reaction:

Feldspar $\longrightarrow$ Clay + (cations in solution), or schematically,

$Fs \rightarrow C + I$, the ions in solution are continually being removed, and the water in contact with the feldspar and the residual clay is continually undersaturated with respect to these ions. In induration, the reverse tendency is operative, that is, water is being expressed mechanically, while the ions tend to remain adsorbed on the clay. The thermodynamic significance of this can be sketched as follows.

If ΔF° is the change in free energy for the reaction

$$C + I \longrightarrow Fs$$

as it occurs in a body of clay, then taking this environment as the standard state gives

$$\Delta F^\circ = -RT \ln K$$

where K is the equilibrium constant of the reaction. Now K may be written approximately as

$$K = \frac{(Fs)}{(C)(l)}$$

where the brackets indicate concentrations. Therefore we have

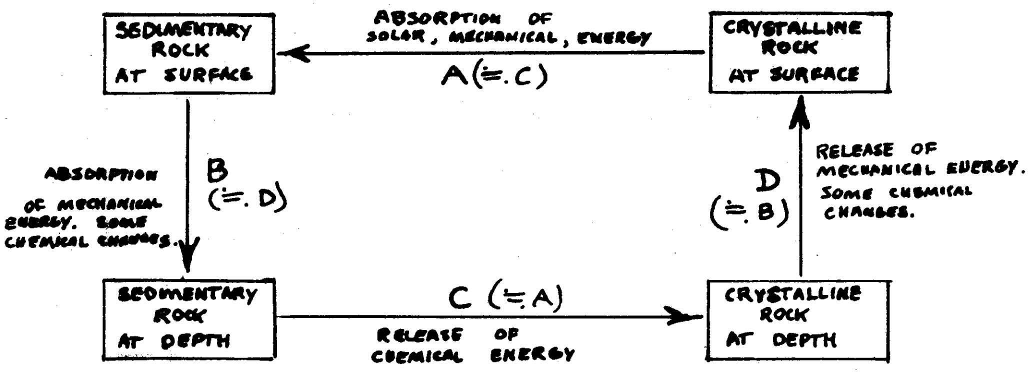
$$\Delta F^{\circ} = RT \ln \frac{(C)(l)}{(Fs)}$$

From this it is clear that even if ΔF° is negative for the clay environment, and the feldspar the favoured form, the ratio $\frac{(C)}{(Fs)}$ may still be large, provided (l) is kept sufficiently small. In weathering, this can be, and is, the case. Experimental evidence of the efficacy of this mechanism of weathering is given by Norton (77).

The above is essentially an application of Le Chatelier's principle. It is of course not necessary that the surface reaction be in equilibrium — indeed it never would be - as long as the equilibrium tendency is operative. In the indurative environment, the expressing of the water would have an effect opposite to the above. This problem is not a simple one, and will not be discussed here, but the sign of the effect is clear. In any case, it has been shown how the apparent anomaly may be resolved. In those cases where pressure favors a certain reaction, in accordance with the equations of page 30, there is again a complicating effect. This would have to be calculated for any particular situation, but, for low pressures, at least, is liable to be of secondary importance.

Another way of considering the problem is to assume that one of the reactions is not truly spontaneous, and external work is being done to achieve it. This would then suggest that the weathering reaction is not spontaneous, since at the surface there is an obvious plentitude of solar, chemical and mechanical energy. (In the above example of clay weathering, work is done to remove the ions in solution, which work is supplied by gravity.) If the anamorphic reaction were considered to be non-spontaneous, we again encounter the problem of the source of the energy. (As mentioned **above**, the pressure effect must be considered, but this is liable to be small. Moreover, it is not plausible to fit such an effect, by itself, into the geologic energy cycle.) A particularly clear instance of the above concept of non-spontaneity is provided by the example of purely clastic weathering. Here there is undoubtedly a difference in sense of the surface and the indurative reaction, but no one would suggest that this difference in sense is anomalous, or that it is fundamentally due to difference in pressure.

The ease with which the concept of chemical energy fits in with the classical geologic cycle is also of appealing simplicity. This has already been mentioned under Solar Radiation, page 10 . The cycle, considering chemical energy, would be similar to:



$$A+B+C+D \doteqdot 0$$

From the point of view that the chemical energy released at depth derives ultimately from solar energy, crustal phenomena would appear to be tuned largely to solar radiation, with the relative rate of mechanical and chemical processes being the significant factor at any point. The effect of energy from the infra-crustal region has not been stressed above, but on this scheme it is possibly rather small. The above cycle may be compared with that given by Barth (4) page 36.

The assumption that in the absence of a surface perturbation, the contribution from the interior is small, receives somewhat tenuous support from the "dead" nature of the moon. The aspect of the moon presented to us is certainly "like nothing on earth". That is, the apparently patternless, cratered, "mountains" may well have attained their present form at the time of the origin of the moon. This suggests that either the moon is of very recent origin, or that it does not possess the mechanism essential to the formation of earth-type features. Aside from the well known differences in size, density, and possibly composition of the moon with respect to the earth, the most fundamental feature is its lack of an atmosphere.

On this basis, even though the moon receives the same amount of solar energy, specifically, the chief tool-i.e., a hydrous atmosphere- by which this energy may be stored is not present. See also later sections on geological implications of chemical energy.

The observed features could also be explained on the basis of rapid cooling of the moon - because of its small size - to the point where primary heat was ineffective. This has been pointed out by Dr. N. Haskell, in a private communication to the author.

GEOLOGIC VALUES OF TRANSFORMATION HEATS

It is clear that every physico-chemical transformation has some heat effect, positive or negative, associated with it. Then, since every known transformation type is represented in geology, a complete list of "geologic values" would be length indeed.

For this reason, only certain transformations which are important in, or peculiar to, metamorphism, will be considered. In any particular case, it must be remembered that more classical reactions such as solution, sublimation, dilution, and their converse have to be included.

Under this plan, the heat effects accompanying the following will be considered:

1. Devitrification
2. Recrystallization
3. Reactions in the ordinary sense.

a. Devitrification

The glassy state is a rarity in physics as a whole, being possible in only one element, selenium, and in a few oxides and oxy-salts. The local importance which this state has in geology is of course due to the glass-forming properties of the silicates.

Present ideas of the glassy state, and the reason for it, are very similar to those first expressed by Zachariasen in his classic paper (127). Briefly, all glasses seem to be characterized by having as primary structural elements certain closely-knit groups, such as SiO_4, BO_3, and PO_4. These join by sharing corners, edges, and faces, but the exact manner in which they do so is of minor importance, as is borne out by the variety of sharing-schemes observed in the crystalline silicates.

Glasses may then be thought of as possessing short-range order - within the structural unit, or through a few units - but exhibiting randomness on a broader scale. Under such a scheme, a glass-former has less excess energy relative to its completely ordered crystalline counterpart than a non-glass-former would have. Nevertheless, the glassy state is a high energy state, and the formation of glass seems in every case to be due to rapid cooling to below the temperatures at which the devitrification rate is measurable.

Excellent recent discussions of the glassy state are given by Weyl (120,A,B); Smekal, (100), and Cox (19a).

In Table II, data on devitrification heats, from several different sources, are tabulated. Where the original reference has given heats offusion, these have been converted to devitrification by 20°C., using the relation (1) of page 41 , and interval heat capacities given in reference (5) section 16.

With regard to this conversion, it must not be assumed that the specific heat of a glass is always greater than that of the corresponding crystal, and that the heat of devitrification is therefore much less than the heat of fusion. This assumption concerning the specific heats is an extension of the so-called Richarz' rule, which assumes that the higher energy form of two modifications always has the higher specific heat. Measurements of White (121), Wietzel (121), and Bridgman (10c) have shown that this rule need not be valid when applied to compounds, and that some glasses have lower specific heats than the crystal

TABLE II

STANDARD ENTHALPY CHANGE ACCOMPANYING DEVITRIFICATION

Material	Comp.	T	ΔH_T	ΔH_T	ΔH_{20}	ΔT_{20}	Ref.
Units		°C	$\frac{\text{kcal}}{\text{mole}}$	$\frac{\text{joules}}{\text{gram}}$	$\frac{\text{joules}}{\text{gram}}$	°C	
Quartz	SiO_2	20.	2.21	154.1	154.1	186.	Wietzel
		20.	2.32	162.3	162.3	196.	Mulert
		20.	6.95	485.4	485.4	480.	Roy
		20.	3.33	233.0	233.0	268.	Bischowsky
Adularia	$KAlSi_3O_8$	20.	-	348.	348.	390.	Mulert
Microcline	$NaAlSi_3O_8$	20.	-	418.	418.	440.	"
Enstatite	$MgSiO_3$	1524.	-	616.	633.	630.	Birch
Wollaston.	$CaSiO_3$	1512.	-	528.	258.	260.	"
Diopside	$CaMg(SiO_3)_2$	1391.	-	430.	383.	380.	"
Anorthite	$CaAl_2Si_2O_8$	1550.	-	440.	675.	650.	"
Leucite	$KAlSiO_4$	20.	-	109.	109.	140.	Mulert
Albite	$NaAlSi_3O_8$	1105.	-	203.	140.	150.	Birch
Rhodonite	$MnSiO_3$	20.	8.52	271.	271.	260.	Mulert
Willemite	Zn_2SiO_4	20.	9.04	170.	170.	190.	"

Key:

Material-	the mineral name of the crystalline phase
Comp.-	the approximate chemical composition of the material
T -	the temperature at which the transition was measured
ΔH_T-	the enthalpy change accompanying the transition at T
ΔH_{20}-	the enthalpy change accompanying the transition at 20
ΔT -	the adiabatic temperature increase attending devitrification of the material at 20
Ref. -	the reference from which the data were obtained

over large ranges. It thus happens that the devitrification heat of quartz glass at low temperatures is nearly equal to the latent heat of fusion.

Calculation of the heat rise due to devitrification at 20°C has been made assuming that the specific heat has a constant, mean, value. It is a simple mathematical exercise to include the change in specific heat with temperature, but the data are not considered accurate enough to warrant this refinement.

The data given are to be regarded as approximate only. A good idea of the variability possible in measurements may be gained by perusal of the notes accompanying the data given in reference (5), pages 237 and 238 .

Particularly striking in the accompanying table is the discrepancy between the values for devitrification of quartz obtained by Ray (86) and those of Wietzel (121) and Mulert (75). Since this point bears on the method of differential heat of solution in general, and also on the surface and strain energy factors which are to be treated below, it will be considered in greater detail.

In discussing the differential heat of solution method, the difference between the techniques of Ray and Mulert was mentioned. Ray's technique was developed as a result of the conviction of Travers (115) that the values of Mulert and Wietzel for the devitrification of silica glass were too low. Travers based his belief on the data of Tschernobaeff and Wologdine (115a), which gave a value of 7.3 Kcal/mole (as against 2.32 Kcal/mole given by Wietzel), as well as upon mistrust of the technique of the earlier workers.

Specifically, Travers felt that extensive grinding, which these authors had to employ in order to achieve rapid solution, had affected the state of the material. (Mulert had ground his material for 17 hours, and then separated the fines via a water process, ending up with one gram of usable material per kilogram of original material. Wietzel ground his material for 100 hours in a mechanical agate mortar.) After obtaining his value of 6.95 Kcal/mole, Ray, working under Travers, checked their assumption as to the error in the original paper by measuring material which had been ground 15 hours, with the results given in Table III.

TABLE III

THE EFFECT OF GRINDING ON HEAT OF SOLUTION

Material	Heat of solution in kilocalories/mole		
State	20-40 mesh	15 hrs. grinding	difference
Quartz glass	37.24	36.95	.29
Quartz crystal	30.29	32.46	2.17

(The above heats of solution are in 35% HF).

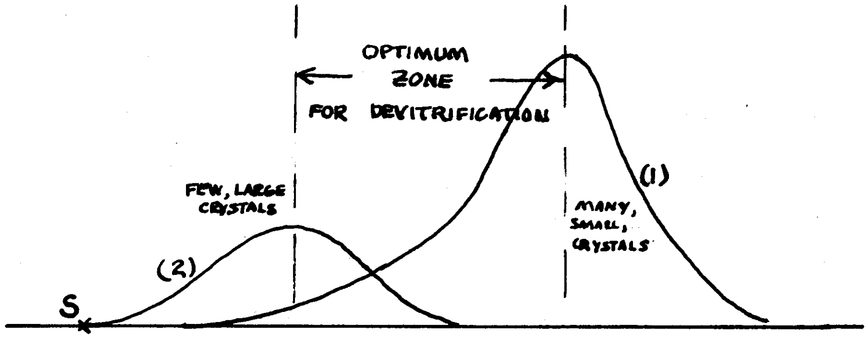
In interpretation, Ray and Travers assumed that grinding had produced partial devitrification of the material, with an according increase in specific energy. They were unable to explain the decrease in energy shown by the glass after grinding, since X-ray work by separate investigators failed to show crystalline material which might decrease the energy.

The present writer feels that there is no real anomaly in the above effect. The factors involved are surface energy and strain energy - which latter is equivalent to the above "partial devitrification". Grinding of quartz crystal is therefore certain to increase its energy, since it must increase the surface area, and also disrupt the low-energy crystalline state. The effect of grinding on the glass is however not so easily predictable. First, grinding might have an annealing action on the glass, and tend to give a rude crystallization too imperfect to be detected by X-ray methods. Second, the specific energy of the atomic complexes near the surfaces may actually be less than the specific energy of volumes within the glass. There is some evidence that rather low-energy configurations - at least relative to the glassy structure - may be realized on crystal surfaces (12). At any rate, grinding is not to be expected to have the same effect upon glassy as upon crystalline material.

A third possibility is of course that there has been experimental error. With regard to this, the above effect was found to be reproducible. As for the general accuracy of the measurements relative to those of Wietzel and Mulert, the following fact is suggestive: the temperature changes actually measured by Wietzel and Mulert in their calorimeters were of the order of one degree centigrade, while with Ray's method, no temperature change was lower than six degrees centigrade, and some were as high as 34°C.

For Ray's figures, the reader is referred to the original paper (86).

Recent discussions of devitrification in the literature are those of Cox (19a) Weyl (120a, 120b), and Gilard (34). The latter gives a qualitative treatment of the factors involved, from the point of view of manufacture. A point made, based upon observation , is that devitrification depends upon both the rate of nucleation and the rate of growth of nuclei once formed. The situation was first stated by Tamman, and can be diagrammed as follows;



DEVITRIFICATION OF GLASS.

S is the melting point, curve (2) is the rate of growth of nuclei, AND CURVE (1) IS THEIR RATE OF FORMATION. See also the experimental work of Swift (106).

b. Recrystallization

By recrystallization is here meant that process by which a crystal aggregate decreases its specific surface area, or by which internal strains are dissipated. That is, a net decrease in surface energy or strain energy is involved. Such phenomena are of course widespread in metamorphism, but are most obvious in monomineralic materials, such as gypsum, limestone, halite, and sandstone.

The underlying principles of this type of re-crystallization have been given by Buerger and Washken (12) as a preface to experimental work on recrystallization of several monomineralic powders. A more lengthy treatment is that of Giesler (32), which applies chiefly to metals. See also some of the authors mentioned in "previous work" page 50 of this paper.

That there is a tendency for crystalline aggregates to minimize their specific surface and strain energies is of course theoretically certain. More important for practical purposes is the experimental fact that such energy actually is capable under suitable conditions of driving the transformation. This is clearly shown by the work of Buerger and Washken mentioned above, and, on a more general scale, by similar sintering experiments in ceramics and metallurgy. Sintering - the welding together of powders of crystals or glasses at temperatures below their melting points - has been used since the earliest times for fabricating metals which could not be melted, as platinum, More recently, powder pressing is becoming increasingly popular in metal processing.

The origin of the compaction tendency is considered to be primarily the excess surface energy of the powder over the compact. See, for example, Mackenzie and Shuttleworth (68). The strain energy is not felt to be so efficacious, at least in metals, because it is less readily stored in the structure. Quantitative measurements on the power of the surface energy in sintering have been made by Shaler and Wulf, (96), with the result that it is considered to be sufficient to explain the observations. A literature review of sintering is given by Rhines (88).

The total surface energy of a mineral grain in any environment is related to the surface tension of the mineral with respect to that environment as follows:

$$E = \int_S T \, dS$$

Where E is the surface energy, T is the surface tension proper to the environment, and S is the surface area of the mineral grain.

Such an equation is quite useless for the practical determination of the surface energy. This is so because direct measurement of T for solids is not possible, and in any case, T would vary from place to place on the crystal surface, in a very complex manner. Hence it is usual to determine the surface energy in ways other than via the surface tension. A few of these are:

1. Direct measurement of surface and strain energy by differential heat of solution, heat of fusion, heat of reaction, ..
2. Measurement of properties which depend on the surface energy or the surface tension, as vapour pressure, solubility rate, ..
3. Calculation of the surface energy from knowledge of the structure and bonding.

Of these three methods, only the first is of any practical use in geology, at least at present.

In principle, energy due to surface area can be determined just as can any structural energy, by differential heat of solution, and other methods of section IIIa. The results of the previous section, regarding the effect of grinding on the energy of quartz, are an illustration of this. Actually, there is a dearth of information on the surface tension and total surface energy of solids, despite the fact that geological values could be readily obtained.

The only direct work on surface energy, done using differential heats of solution seems to be that of Lipsett et al (65). The mineral investigated was halite, suitably purified. A water calorimeter was used, and in the later experiments, special features were developed to minimize the error due to hygroscopic water. Two forms of halite were used for the fine sample - salt prepared by sublimation, and salt prepared by grinding. The sublimate sample had 12.1 calories/mole excess energy over the coarse material, and the ground sample had 30 calories/mole excess energy. Surface area calculations were made, probably with doubtful accuracy, and gave a value for the specific surface energy of 400 ergs/cm2.

Utilization of method 2. is difficult, and of doubtful significance. It is necessary to develop equations expressing the relation of solubility, or vapour pressure, -- to the surface tension, which is of itself difficult, and then measure differences in rate of solubility, vapour tension and the like. For solids this is again a difficult task. Equations have been developed by Dundon and Moch. (21).

They have worked on $CaSO_4$, and, although obtaining no usable values, states that the surface tension varies directly as the hardness of the crystal, and inversely as the molecular volume. Their paper illustrates the complexity of the method well, which method is far too roundabout for geological purposes. (It requires a knowledge of surface area, to get total energy values, as well as having the above mentioned shortcomings).

The third method depends of course on a knowledge of the nature and energies of the bonds in the crystal, and is subject to the same shortcomings mentioned in section IIIa., in referring to cohesive energy. Besides the surface energy, even for isotropic crystals, varies very greatly with the nature of the atomic planes forming these surfaces, and calculations are also complicated by edge effects impossible to treat accurately. All in all, such calculations are more useful as checks on the theory of cohesion used, than as a method of obtaining values. This is particularly so in the case of silicates. Some calculations have been made for ionic crystals - for molten halite, there is a fair check with experimental values. For halite crystal, and the {100} surface, the values of 150 and 900 ergs per cm^2. were obtained by different workers. The rough agreement with the above value of Lipsett is probable fortuitous. For additional data see Seitz (94) page 98.

The.above values for halite would give adiabatic temperature rises for only a few degrees. Moreover, the relation of the measured transformation to any geological transformation is questionable. The values and temperature rises are summarized in Table IV below. Because of their much more tightly bound structure - evidenced in greater hardness and density - the silicates would be expected to have greater specific surface and strain energy for the same degree of comminution.

TABLE IV

ADIABATIC TEMPERATURE RISE DUE TO RELEASE OF CERTAIN SURFACE AND STRAIN ENERGY

Material	Energy/mole in calories	Source of Data	Temperature Rise in Degrees C
NaCl sublimate	12.	Lipsett (65)	1.0
NaCl ground	30.	"	2.5
ZnO	1,150	Hedvall (43)	120.
Fe_2O_3 (hematite)	4, 700	" "	185.
Quartz	2,170	Ray (Table III)	180.
Quartz	4,740.	Ray (page)	370.
Chalcedony	3,070.	Wietzel (121)	245.
Colloidal SiO_2	5,330	Bischowsky (6)	390.
Colloidal SiO_2	8,870	"	580.
Amorphous Fe_2O_3	13,500	Frick (29)	425.

The order of magnitude of the surface and strain energy suggested by the work of Ray would seem to confirm this. This work has already been mentioned (p. 67). If the total difference between Ray's value for the devitrification of silica and Mulert's is due to surface and strain energy, the surface and strain energy is then 4.74 Kcal/mole. Such an energy change would lead to an adiabatic temperature rise of about 370°C.

Relative to considering the heat effect of colloidal silica as being due entirely to surface energy, there is also the possibility that the silica is not in the form of quartz, but in a higher energy form, as cristobalite - e.g. see Buerger (12). The effect here would be small, however, and in any case the only important point is that colloidal silica does occur geologically.

Fricke and Klenk (29) have determined the heat of the transition: amorphous $Fe_2O_3 \rightarrow \alpha\ Fe_2O_3$. The adiabatic heat rise would be about 425°C , using their value.

Finally, a rough estimate of the surface energy of ZnO and Fe_2O_3 can be obtained from the data of Fricke and Gwinner (29A), whose work has already been cited. The figures given in the table are maximum ones, calculated from the heats of solution given by the above workers. The adiabatic rise is calculated using specific heats given in the Chemical Engineering Handbook. It is interesting to note that the energy is higher for the harder crystal - assuming the forms are zincite and specularite. However, since data on the surface area is not available, it is unwise to speculate further on this point.

The values in the table are of course qualitative only, and depend on the state of the material. In any particular case, the values would of course change. The purpose of the table is merely to convey an idea of the magnitude of the surface and strain effect.

From the above it is seen that there is an almost complete lack of total surface energy data. In view of the ease with which reasonably good values could be obtained for soluble minerals, this is rather anomalous. Besides being easy to work with, such materials as calcite of various degrees of fineness, aragonite, dolomite, magnesite,... would afford data of ready geologic application. This is because the transformations involved occur in rather low grades of metamorphism, in which conditions of temperature, stress, and even times involved may be well known or approximated. With knowledge of the various parameters, it might be possible to estimate the rate of the reactions, and the effect on the thermal gradient.

For silicates, the measurement is of more difficulty, and the results of somewhat less ready applicability. However, the order of magnitude of the changes should certainly be measured.

Quite aside from the values of surface energy, it is appropriate to list here some recent values of the surface areas of certain geologic materials. Surface areas in the following table are given in square meters per gram.

TABLE V

SURFACE AREA OF CERTAIN MATERIAL IN SQUARE METERS PER GRAM

No	Material	Area	No	Material	Area
1.	Fine red silt	2.	10.	$BaSO_4$ ppt.	4.30
2.	" inorganic limestone	40.	11.	Montmorillonite and kaolinite	15.5
3.	Deep water red clay	25.			
4.	" " green "	10-15	12.	Cecil soil 9418	32.8
5.	Mica (0.1mm sheets)	.02	13.	Halloysite	43.2
6.	$CuSO_4.5H_2O$ (40-100 m)	.16	14.	Illite	97.1
7.	KCl (200 mesh)	.24	15.	Silica gel	584.
8.	Pumice	.38	16.	Darco G	2123.
9.	Cement	1.08			

(The above data are from Kulp and Carr, reference 55 .

c. Reactions in the ordinary sense.

It is difficult to obtain accurate values of the heat effects attending geologic reactions, not only because of lack of heat data for geologic materials, but also because the nature of the reactions - reactants, state, and mechanism - is frequently in doubt.

The first lack of knowledge can be repaired by application of research methods now known, as described in section III, page 38. The second point is more fundamental, and requires a closer study of the basis of metamorphic and diagenetic processes, with particular regard to the nature and origin of the reactants.

There is not sufficient accurate data to warrant detailed discussion or calculation. However, it is worthwhile to classify briefly the reactions of interest before presenting such data as is available. Thus the reactions may be separated roughly according as they occur in one or another of the following regions:

1. Earth's surface. (Includes reactions of katamorphism, as solution, hydration, oxidation,...)
2. Crustal layers.
    a. Sedimentary rocks. (Reactions involving salts and clays, for the most part, and including hydrations, dehydrations, syntheses,... i.e. anamorphic reactions generally.)
    b. Igneous rocks. (Including hydrations, phase changes, decompositions for the most part.)
    c. Ores (replacements, decompositions, hydrations, ...)
3. Infra-crustal. (Transformations involving silicates, at least in the mantle. Below the mantle, unknown.)

As already stated (page 17), heats of reactions occurring at the surface are usually so swamped by the effects of solar radiation and ordinary climate as to be without significance for the temperature of that region. In certain areas, temperatures and micro-climates may be considerably affected by vigorous oxidation and the like, but the above statement is essentially true.

At the other extreme, nothing is known of reactions in the mantle and core, and despite their possible importance for these regions, they cannot be considered here. It is thus the reactions of the crustal layers that are of principal interest.

Reactions involving salts, sulfides and oxides, and silicates, respectively, are discussed below. The few reaction heats given are not presented as a complete listing. There are many subsidiary reactions which could be approximated with data now available. However, for the present purposes, the following is felt to be a reasonable presentation.

1. Salts.

The difficulty in attempting to determine the heat effects arising in reactions between salts, in the diagenetic environment, is again that of writing the actual reaction. The systems concerned are usually definitely open, which affects both the equilibrium obtaining, and the enthalpy change. Because the heat of reaction for the closed system may be rather modest, subsidiary heat effects are important, and it is difficult to make predictions. Of the reactions listed in the accompanying Table VI, perhaps only 1, 2, and 4 are reasonably correctly written.

TABLE VI

ENTHALPY CHANGE AND ADIABATIC T RISE IN CERTAIN SALT REACTIONS

	Reaction	$-\Delta H$ (kcal)	ΔT (°C)
1.	$CaMg(CO_3)_2 \nrightarrow CaCO_3 + MgCO_3$	-2.2	-60.
2.	$CaSO_4 + 2H_2O \longrightarrow CaSO_4.2H\ O$	5.0	110.
3.	$2CaCO_3 + MgSO_4 \longrightarrow CaMg(CO_3)_2 + CaSO_4$	.21	4.
4.	$CaCO_3$ (aragonite) $\longrightarrow CaCO_3$ (calcite)	-.04	-2.

The reaction aragonite-calcite is endothermic, as noted. Its observed occurrence does not necessarily refute the statements of page 25. In this case, the heat effect $-\Delta H$ is sufficiently modest for the entropy term $T\Delta S$ to overcome it and make calcite the stable form at rather low temperatures. The higher density of aragonite would suggest that it has the lower entropy, which is consistent with the above.

2. Ores.

The same difficulty, that of writing down reactions that actually occur, and not merely ones for which heat data are available, presents itself here. Exceptions to this statement arise in the presence of a number of phase modifications in ores, such as high to low chalcocite. However, such reactions are of limited scope, and the reaction heats are moreover usually small.

Oxidation reactions on ores have been discussed by Lovering (66) and Emmons (25). The reactions they have used are given below.

No attempt has been made by this writer to investigate the validity of these reactions.

TABLE VII

STANDARD ENTHALPY CHANGE AND T RISE IN OXIDE AND SULFIDE REACTIONS

Reaction	$-\Delta H$ (kcal.)	T (C)
$Al_2O_3 + 3H_2O \longrightarrow Al(OH)_3$	22.9	620.
$2Fe(OH)_3 \longrightarrow Fe_2O_3 + 3H_2O$	-9.1	116.
ZnS (wurtzite) $\longrightarrow$ ZnS (sphalerite)	3.19	250.
$2FeS_2 + 15O + (n+7)H_2O \rightarrow 2Fe(OH)_3 + 4H_2SO_4 + n\ H_2O$	343.	--

Silicates.

Silicate reactions are by far the most important for the purpose of this paper. This is because of the pre-eminent position which such reactions occupy in metamorphism, and also because both theory and observation indicate that the heat effects attending silicate reactions are much higher than for corresponding salt and sulfide reactions.

Direct heat data has been located for only one important metamorphic reaction: that of kaolinite to sillimanite, quartz, and water. There are available a number of heats of reaction for the formation of silicates from the oxides, both experimentally determined and calculated from structure energy. These are interesting in suggesting an upper limit for geologic heats of formation, but have otherwise

TABLE VIII

STANDARD ENTHALPY CHANGE FOR CERTAIN SILICATE REACTIONS

No.	Reactants	Products	-ΔH (kcal)	Ref.
A.				
1.	Al_2O_3 + SiO_2 alumina quartz	Al_2SiO_5 sillimanite	40.4	Bischow.
2.	CaO + SiO_2 lime quartz	$CaSiO_3$ wollastonite	27.7	"
3.	K_2O + Al_2O_3 + $6SiO_2$ potash alumina quartz	$2KAlSi_3O_8$ adularia	117.9	Mulert
4.	K_2O + Al_2O_3 + $6SiO_2$ potash alumina quartz	$2KAlSi_3O_8$ microcline	90.9	"
5.	Na_2O + Al_2O_3 + $4SiO_2$ + H_2O soda alumina quartz water	$2KAlSiO_4$ leucite	93.0	"
6.	CAO + Al_2O_3 + $6SiO_2$ + H_2O lime alumina quartz water	$CaAl_2Si_6O_{16}5H_2O$ heulandite	46.2	"
B.				
7.	CaO + H_2O	$Ca(OH)_2$	16.0	Bischow.
8.	Na_2O + H_2O	$2NaOH$ xal.		"
9.	Na_2O + H_2O	$2NaOH$ (∞H_2O)	46.0	"
10.	Al_2O_3 + H_2O	$2Al(OH)_3$	22.9	"
11.	CaO + CO_2	$CaCO$ (calc.)	43.3	"
12.	K_2O + H_2O	$2KOH$ xal.	49.8	"
13.	K_2O + H_2O	$2KOH$ (∞H_2O)	62.7	"
C.				
14.	$2Al(OH)_3$ + SiO_2 quartz	Al_2SiO_5 + H_2O sillimanite	17.5	above
15.	$Ca(OH)_2$ + SiO_2 quartz	$CaSiO_3$ + H_2O wollastonite	11.7	"
16.	KOH + $Al(OH)_3$ + $3SiO$ xal. quartz	$KAlSi_3O_8$ + H O adularia	22.2	"
17.	KOH + $Al(OH)_3$ + $3SiO_2$ (∞H_2O) quartz	$KAlSi_3O_8$ + H_2O microcline	16.1	"
18.	$NaOH$ + $Al(OH)_3$ + $2SiO_2$ (∞H_2O) quartz	$NaAlSi_2O_6 \cdot H_2O$ analcite + $3H_2O$	3.7	"
19.	$CaCO_3$ + SiO_2 calcite quartz	$CaSiO_3$ + CO_2 wollastonite	-20.5	"
C.				
20.	$H_4Al_2Si_2O_9$	Al_2SiO_5 + $2H_2O$ sillimanite + SiO_2 quartz	26.0	Klever

little or no petrologic significance. These reactions are listed in part A of the accompanying table VIII.

Most of these reaction heats have been determined by Mulert(75), as indicated. Because of the difficulty of dissolving the silicates in HF, which solution is the basis of the determination, the values given are undoubtedly considerably in error. This is certainly suggested by the large discrepancy between the heat of formation of microcline and adularia. Besides being subject to such errors, it is obvious that the reactants do not represent naturally-occurring minerals. The sole exception to this is the reaction between Al_2O_3 and SiO_2 to form sillimanite. All of these do occur naturally, and corundum is frequently associated with quartz in modern sands. The adiabatic rise in temperature for this reaction would be approximately 1000°C. However, the source of this energy is not attributable to weathering, but to the source which formed the parent rocks.

For the others, hydration of the oxides will greatly cut down the heat of reaction. In actuality, the reactants for the formation of, say, authigenic feldspar, are some sort of illitic clay-material, with indefinite structure and composition. The real transformation then probably cannot be even approximated by measurement on non-geologic material. The effect of this hydration is included in parts B and C of the table. Of these equations, only equation 11 seems to have any geologic significance directly.

The moderating effect of water should not be surprising:

a similar effect occurs when an electrolyte is dissolved in water. That is, considering ionization of NaCl, for example, the heat absorbed by the anhydrous reaction:

$$NaCl \longrightarrow Na^{+} + Cl^{-}$$

is about 190 Kcalories. If water took no part in the reaction, one mole of NaCl in a liter of water would lower the temperature about 190°C. The observed effect is only a few degrees.

The moderating effect in the present case would not be expected to be as large as indicated in part B of the table, because it is unlikely that the heterogeneous geologic material would acheive such a low energy state as the above hydroxides. This would certainly be true once the material had been somewhat compacted. The effect of water is more correctly indicated by the data of Klever, which is discussed below.

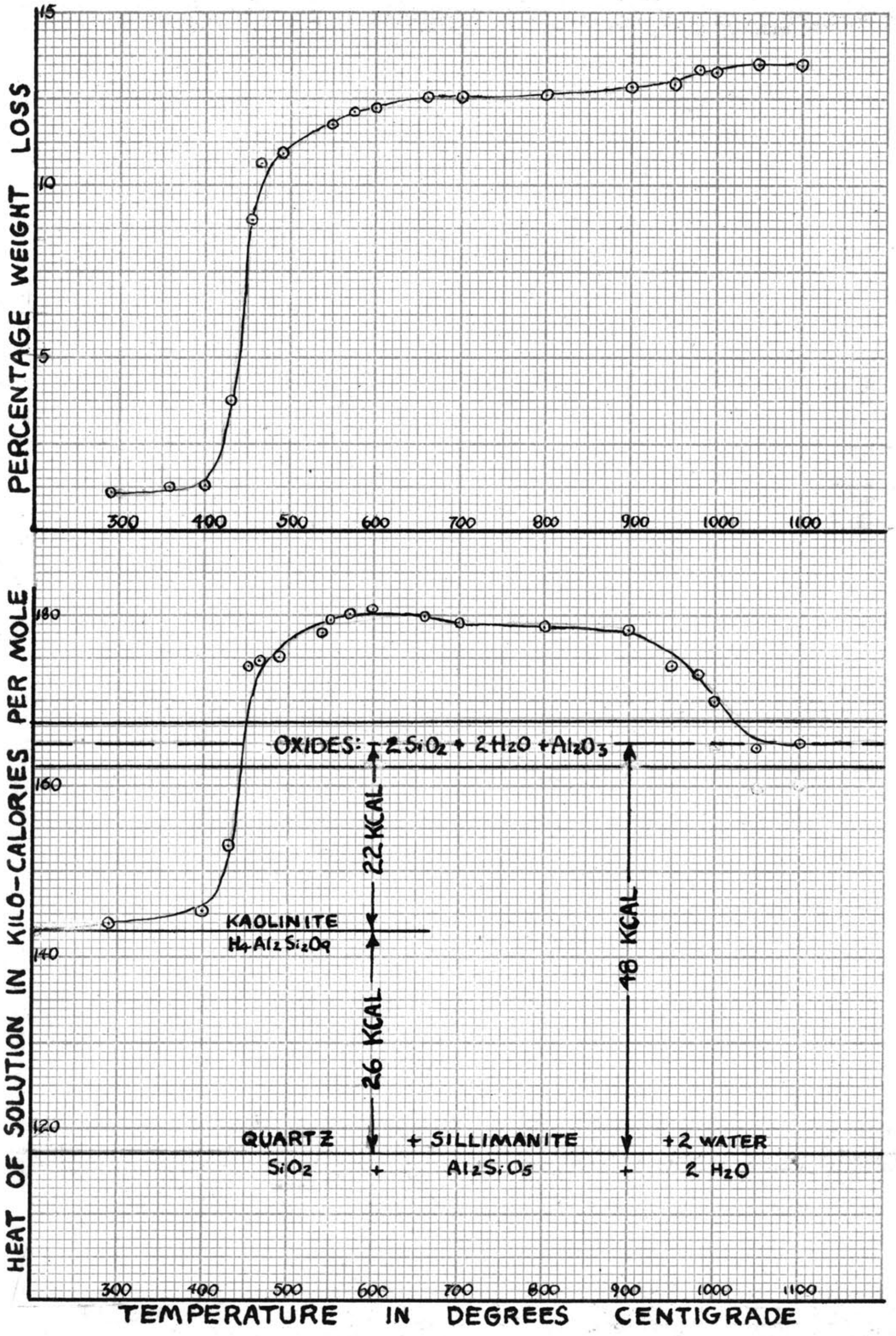
The fact that equation 19 of table VIII (the formation of wollastonite out of silica and calcite), is endothermic, is not detrimental to the general hypothesis. This is a typical contact metamorphic reaction, and in the great majority of instances of its occurrence, the source of the requisite energy is readily visible. Indeed, the fact that wollastonite is not a mineral of "regional" metamorphism supports the contention that the production of such regional metamorphic menerals is ordinarily exothermic. Contributing to the realization of reaction 19 is of course the removal of the gaseous product CO_2. See page 26.

Klever (59B) determined his heat values from differential heats of solution in 40% HF. The material used was Zettlitzer kaolin, stated to be 98.5% pure. The impurities were disregarded in the calculations, and the ideal formula $H_4Al_2Si_2O_9$ used. Dehydration was acheived by heating for 6 minutes in an air stream dried with sulfuric acid and phosphorus pentoxide. Final values used in the determinations are the mean of two or three determinations. From the data given in the original paper, the maximum deviation from the mean is of the order of one or two percent. The effect of the water content on the solution heat is small - of the order of 0.5 kilocalories per mole, from Klever (59B) - and may be disregarded.

Study of the thermal changes accompanying the heating of kaolin, which was the object of Klever's paper, is of little direct interest here. However, his results are an indication of the elegance of the method, and are reproduced in the accompanying Plate I. It is immediately apparent that the curves correctly reflect the well-known structural changes which occur in kaolin at about 550° and 900° Centigrade. The configuration of the heat of solution curve is actually due to structural change, and not merely to water content, since the heat of solution of water is negligible (see above).

From the continuity of the curves above 550°C., Klever concluded that there is no structural breakdown of kaolin at this point, as some investigators had assumed. Rather, there was felt to be support for the existence of a new compound, metakaolin, ~~This had been suggested~~

PLATE I. HEAT OF SOLUTION OF DEHYDRATED KAOLIN (AFTER KLEVER)



This had been suggested by a number of other workers, from X-ray data - e.g. Hyslop (47A). The assumption of metakaolin has been criticized by Eitel (23) and by Sosman (101A). Eitel concludes that there is no basis for such a compound. It is not necessary to take sides on this question, but in support of Klever's work, it should be noted that recent work by Comeforo et. al. (19) has tended to substantiate the existence of metakaolin. Comeforo, using X-ray analysis and electron microscopy, concludes that there is evidence for the existence of "a uniquely organized, non-crystalline compound for which the name metakaolin or pro-mullite seems fully justified."

From the curves, the following heats of reaction are obtained:

$2H_2O + Al_2O_3 + 2SiO_2 \longrightarrow H_4Al_2Si_2O_9$

$Al_2O_3 + SiO_2 \longrightarrow Al_2SiO_5$ (sillimanite)

$H_4Al_2Si_2O_9 \longrightarrow Al_2SiO_5 + 2H_2O + SiO_2$

The value for the heat of formation of sillimanite is in some disagreement with the value listed by Bichowsky and Rossini from Neumann's earlier work, but not inordinately so.

The results for the heat of formation of kaolin from the oxides is in fairly good agreement with the result (18 kilocalories per mole) obtained by Schwiersch (96A).

Superposed on the reaction effect is the effect of surface energy, which was not considered by Klever. As a first approximation, this effect has been ignored, which assumes that the fineness affects all particles similarly. If the fineness of all particles were the same, the heat of solution of the harder silicates would be expected to be increased, and the exothermic effect for sillimanite formation from kaolin would therefore also be increased. If the kaolin is the finer material, then the greater surface might counterbalance this effect. All in all, the best course at present is to ignore the surface effect when writing the values. In further experimental work of this sort, the surface and strain energy should be considered.

Assuming adiabatic conditions, the above value for the reaction:

$$\text{Kaolin} \longrightarrow \text{sillimanite} + \text{quartz} + 2H_2O$$

gives a temperature rise of about 340°C. This includes the water as a product, but does not consider latent heat effects of the latter. The water would be above its critical pressure in most cases. If the effect of water is neglected - which assumes it eventually reaches the surface at surface temperature - the adiabatic rise is about 420°C.

d. Discussion

In summary of the above results, it may be said that a number of geologically important exothermic reactions have been demonstrated.

There is no doubt of the exothermic effect of devitrification. (This is, however, not a primary source of energy, since the material must first have been fused.) There is also no doubt of the sign of the heat effect in recrystallization. For reactions, the case is not so clear, and some minor reactions, at least, are endothermic. For others, data available indicates that they are exothermic. It may be argued with good reason that the present data is not sufficiently accurate to be of significance. However, most of the geologically significant reactions given above appear to be exothermic, and thus the onus of proof passes to those who would assume endothermic reactions.

In the writer's opinion, the only scientific approach at this stage is to initiate research on the heats of reaction, with the stipulation that natural materials be used wherever possible.

B. Transformation Rates.

From the preceding pages, it will be apparent that, because of the complexity of the factors which can influence rates of reactions, it is not possible to write down simple, definite values for the rates of geologic ractions. Rocks are, ultimately, extremely inhomogeneous bodies, and it is to just such inhomogeneities as rocks display that reaction rates are most sensitive.

For this reason, the writer has made no attempt to collect large numbers of values for reaction rates. The few values that are given will indicate the general type of data available. The works of Jost (52), Jander (50), and Hedvall (42A) are the best sources of further values. The values which are given here have been determined from work on :

(i) Single interfaces
(ii) Mixtures of powders
(iii) Geologic data.

(i) A large number of reactions have been studies with reactants in the form of slabs pressed together. In these cases, once reaction has begun, succeeding reaction can only take place by diffusion of the reactants through the product layer. Jagitsch (49) studied the reactions ($MgO + Ag_2SO_4$), ($MgO + Ag_3PO_4$), ($MgO + Mg_2P_2O_7$), and ($MgO + MgSiO_3$) in this manner. He found that the rate of reaction was independent of the thickness of the product layer. He was able to express his results in the form:

$$\frac{dm}{dt} = C e^{-q/RT}$$

where $\frac{dm}{dt}$ is the rate of reaction in gram moles of MgO per square centimeter of contact per second, and C , q are constants. The results are:

TABLE IX

DATA ON RATES OF SOLID STATE REACTIONS STUDIED BY JAGITSCH

Rate expression: $\frac{dm}{dt} = C e^{-q/RT}$

No	Reaction	q (kilocalories)	C gm.-mol. MgO $cm^{-2} sec^{-1}$
1.	$MgO + Ag_2SO_4$	61	2.0×10^5
2.	$MgO + Ag_3PO_4$	61	2.0×10^6
3.	$MgO + Mg_2P_2O_7$	82	2.0×10^5
4.	$MgO + MgSiO_3$	112	1.0×10^6

(ii) Determination on mixtures of powders are of more direct geologic significance than are the above type. As would be expected, rates depend on particle size, and intimacy of contact. Jander (50) has developed the mathematical relation between particle size and reaction rate. His equation does not apply to slow reactions. For these, Segawa (94) has calculated a corresponding relation, by assuming that the rate is entirely diffusion-controlled. The final form obtained by him may be written:

$$\frac{dx}{dt} = k(1-x)^{1+A} \quad \text{with} \quad k = \left(\frac{e^{B}}{1+A}\right) e^{-q/RT}$$

Here, x is the fraction of the material reacted at time t and A, B, q are constants.

Using this equation, reaction rates were determined by thermal analysis studies on a number of powders. A few of the values are:

TABLE X

REACTION RATES FROM THERMAL ANALYSIS OF MINERAL POWDERS (SEGAWA)

Rate expression: $\frac{dx}{dt} = k(1-x)^{1+A}$; $k = \left(\frac{e^{B}}{1+A}\right) e^{-q/RT}$

No.	Reaction	$\frac{e^{B}}{1+A}$	q (kcal./mole)
5.	$CaO + SiO_2$		71.2
6.	$CaSiO_3 + CaO$		61.1
7.	$Al_2O_3 + SiO_2$		40.
8.	$MgO + Fe_2O_3$	$10^{12.86}$	75.3
9.	$CrO + Fe_2O_3$	$10^{14.6}$	84.3

(iii) As mentioned on page 85, geologic occurrences can provide data on reaction rates if sufficient is known of the geologic history. As an illustration of this, the data given by Moore (74) on authigenic feldspar in the Green River shale is hereby considered.

Moore states that the maximum length of the rhomb-shaped crystals is about 3 millimeters (measured on the diagonal) and the average length about .15 millimeters. The width of the crystals was about one third the length.

Now if we assume a rate of the form

$$\frac{dn}{dt} = C e^{-q/RT}$$

where $\frac{dm}{dt}$ is the number of moles reacting per unit time per unit volume, and C , q are constants, we have approximately

$$\frac{\Delta m}{\Delta t} = C e^{-q/RT}$$

This of couse asames constant temperature, and the form the the rate ignores the effect of dis~~s~~appearance of mass.

Assuming that the crystals are in the form of rectangular parallelipipeds, then it is easily comuted that:

a. For the maximum size crystal $\Delta m = 3 \times 10^{-6}$ MOLES
b. For the average size crystal $\Delta m = 4 \times 10^{-9}$ MOLES

Now the Green River formation is Middle Eocene in age, and taking this age as 60 million years, the elapsed time is approximately 2×10^{15} seconds. It is now necessary to estimate values of q and T , in order to compute C . These estimations, together with the resultant values of C , are given in table XI below. The results show primarily the sensitivity of the computed changes in q and T , and no particular best choice is suggested. Rather the point is that with reasonable assumptions, a very large range of values of C is possible.

The unit to be used for C requires some comment. In order to use the size of the crystals as an indicator of the amount of reaction, the "density" of crystals in the rock should be known, as well as the original composition of the rock. Here, it will be assumed that the material for each crystal has come from a cell of one cubic centimeter volume surrounding it. The "unit volume" in the above equation is therefore one cubic centimeter. This would assume that, if the concentration of feldspar-forming material had been homogeneous, there would be one crystal per cubic centimeter. This is probably excessive, as far as the actual occurrence is concerned. Without knowledge of the original concentration, however, this is a fair assumption, and in any case, the real sensitivity of C is not to this assumption of unit volume, or to the assumption of crystal size, but to choice of ε and T. This is apparent from the tabulated results below.

TABLE XI

APPROXIMATION OF FREQUENCT FACTOR FROM DATA ON AUTHIGENIC ALBITE

No.	Δn gm.-mol.	Δt sec.	$\Delta n/\Delta t$ mol./sec.	T °C	T °K	ε kcal/mol	C text
10.	3×10^{-5}	2×10^{16}	1.5×10^{-20}	127.	400.	40.	$1.5 \times 10^{1.5}$
11.	↓	↓	↓	77.	350.	"	1.5×10^{5}
12.				27.	300.	"	1.5×10^{8}
13.				127.	400.	60.	1.5×10^{12}
14.				77.	350.	"	1.5×10^{17}
15.				27.	300.	"	1.5×10^{23}
16.				127.	400.	80.	1.5×10^{23}
17.				77.	350.	"	1.5×10^{29}
18.				27.	300.	"	1.5×10^{37}
19.				127.	400.	100.	1.5×10^{34}
20.				77,	350.	"	1.5×10^{42}
21.				27.	300.	"	1.5×10^{52}

(For the smaller crystals, $\Delta n = 4 \times 10^{-9}$ mole, and C is $4/3 \times 10^{-4}$ of the corresponding value given above)

VI. MATHEMATICAL FORMULATION

A) Implications. A necessary preliminary to mathematical formulation of any problem is a knowledge of the type of phenomena which is to be described. As elementary as this condition may seem, it is only rarely that we are able to meet it, where geological problems are concerned.

With regard to the present problem, we are interested in the interplay of reaction rate and heat dissipation in geologic bodies. The variety of factors which influence reaction rate have already been mentioned. Here, it is desired to point out the uncertainty which surrounds the method of heat transfer.

It is usual to assume that heat conduction in the mantle and lithosphere is by conduction. This is partly because of evidence for the general solidity of these regions, and partly because of the simplicity of the mathematics of conductivity relative to that relating to other modes of heat transfer. In this paper, the conductivity equation will again be used, but other possibilities must be mentioned.

In the first place, fluids are present in many geologic bodies, either intergranularly or in fractures, and here mass transfer by convection must far exceed conduction. Again, in the mantle, there is the possibility of convection despite the high viscosity of the material involved, and in this case heat transfer by conduction would be far outweighed - see Pekeris (80). There is also energy flow associated with mass transfer by diffusion, and under certain conditions, energy transfer may be by nuclear ("lattice") vibration rather than by electronic excitation. Radiation will also be effective in unique circumstances.

All in all, the conductivity equation probably holds rigorously in few cases. Nevertheless, it provides at least a useful frame of reference. Also, many of the variations in mechanism of heat transfer can give rise to local or bulk equations which are not significantly different in form. The conductivity equations would then apply, with the variations accomodated by changes in the parameters.

Simplified treatments of situations involving other modes of heat transfer could be used where the conductivity assumptions are obviously wrong, but such will not be attempted here.

B) The Heat Conduction Equation - The equation for conduction of heat in a solid in which no heat is being generated is

$$\rho c \frac{\partial v}{\partial t} = \operatorname{div} (K \operatorname{grad} v) \qquad (1)$$

where

v is the temperature of the solid at P (x, y, z).

ρ is the density of the solid at P (x, y, z)

c is the specific heat . . . . .

K is the conductivity . . . . .

t is the time.

This equation is valid even if the medium is homogeneous and anisotropic.

If the solid is isotropic but not homogeneous, then (1) becomes

$$\rho c \frac{\partial v}{\partial t} = \frac{\partial}{\partial x}\left(K \frac{\partial v}{\partial x}\right) + \frac{\partial}{\partial y}\left(K \frac{\partial v}{\partial y}\right) + \frac{\partial}{\partial z}\left(K \frac{\partial v}{\partial z}\right) \qquad (2)$$

If the solid is homogeneous and isotropic, (1) becomes

$$\rho c \frac{\partial v}{\partial t} = K \nabla^2 v \qquad (3)$$

Finally, if heat is generated in the solid so that at the point P (x,y,z), heat is supplied at the rate $S(x,y,z,v;t)$, the equation for conduction is

$$\rho c \frac{\partial v}{\partial t} = K \nabla^2 v + S(x,y,z,v,t) \tag{4}$$

Note that, besides the case of chemical change within a body, (4) is applicable to such common cases as the production of hat by electic current, by absorption of radiation, and by radioactive decay.

C) Application of the heat flow equation to geology - In every practical application of the heat flow equation, certain idealizations of the problem under consideration are necessary. In geology, this situation may become extreme.

With respect to the general equation (4), geologic application involves assumptions as to:

1. The geometry of the bodies being considered.
2. The nature of the parameters.
3. The boundary conditions.
4. The initial conditions.

These points will now be discussed briefly.

1. Simplification of the shape of the geologic bodies involved is not peculiar to application of the heat flow equation, but is necessary to every mathematical formulation of problems concerning

geologic bodies. For the most part, this paper isconcerned with heat flow in stratiform media bounded on one side bythe air surface, and on the other by an inert medium. This situation is usually taken to be described by a semi-infinite slab. In describing any particular geologic situation this approximation may be quite erroneous, but as a framework for qualitative discussion, it is adequate. Given solutions for such simplified cases, the effect of actual complications can be estimated.

2. Data concerning the value and nature of the parameters K, C, and ρ would be required for the exact solution of the equation. In practice, these are considered to be temperature-independent, which is, of course, not so rigorously, even in the case of non-geologic material. In geology, there may be variation of K and C with temperature amounting to several orders of magnitude for the range of temperature encountered in metamorphism. This is because of the effect of the large number of phase changes, reactions and allied phenomena definitely occurring when rocks are subjected to changing physical conditions.

For simple variations of K and C with temperature or position, solution of the equation is in some cases still possible, but treatment of many of the actual variations, even if the form were known and expressible, is definitely not feasible using ordinary mathematical methods. Again, the solutions which are obtained on the simplified basis must be taken only as a guide to the effect of the actual variations.

Further assumptions regarding K, ρ and c which are usual are that the medium in question is isotropic, that is that the parameters are the same no matter which direction of heat flow is considered; and that the medium is homogeneous, that is that for any particular direction, each parameter has the same value at all points.

Assumptions regarding the nature of the source will be discussed later.

3. One of the most important points with respect to equation (4) which must be decided for any particular problem concerns the nature of the boundary conditions. The conditions usually employed are:

1. Prescribed surface temperature.
2. No heat flow across the surface.
3. Prescribed heat flow from the surface.
4. Radiation at the surface.
5. Boundary separates two solid media of different properties.

Depending on the shape of the body, conditions such as the above have to be satisfied at one or more surfaces. The case of the infinite medium, which has very real significance for some geologic problems, as where the boundary is far away relative to the region of interest, requires aless usual type of condition, e.g. that the temperature is never infinite. This type of boundary condition is much less simple to work with.

Deciding on the boundary conditions for certain surfaces of geologic interest is quite simple - for instance condition 1 or condition 4 might be applied to the free (air or water) surface of a body. Other cases cannot be adequately described without making what are often very fundamental assumptions regarding earth processes. A case in point is the lower boundary which a sedimentary series has with, say, a crystalline basement. Here, making a choice of one of the boundary conditions immediately implies knowledge about the heat flow from below, knowledge which we certainly do not possess. Again, the best method of attack is to consider certain simple cases, and from a study of the ensuing results to estimate the effect which actual variations might have.

4. Imposing initial conditions involves less extrapolation from actual knowledge than boundary conditions demand. A considerable amount is known about depth - temperature relations in geologic localities, and reasonably correct assumptions can be made. In any case, it is often not difficult to obtain solutions for various initial conditions once the solution for one type is known.

In summary of the above remarks, it is clear that any equation such as (4) may be quite misleading in certain cases of geologic importance. Extremely detailed calculations are therefore not always desirable, even where possible, and to any solution must be appended an estimation of its field of significance. Further discussion of the assumptions necessary is given along with the individual problems considered later.

D) The source function - The possibility of solving equation (4) is intimately connected with the form of the source function, S. Briefly, the situation is as follows:

1. If S is constant, the equation can be reduced to the source-less form by a substitution.
2. If S is independent of temperature, three general methods can be used:
    a) Integration of source solutions, (Green's method).
    b) Integral transform methods.
    c) Reduction to homogeneous form by change of variable.
3. If the solution for the time-independent source is known, that for the time-dependent source can be obtained from Duhamel's theorem (see below).
4. If S is a linear function of temperature, the equation (4) remains linear, and may be reduced to the source-less form by substitution.
5. If S is an arbitary function of temperature, the equation is intractable as far as ordinary analysis is concerned.

Chemical sources, of the type to be considered here, have of course, a complicated temperature dependence, and hence fall into the category 5 above. The form of the source function is discussed elsewhere (p 28). It should be noted here however, that $\int_0^\infty S\,dt \lesssim Q$ where Q is the total heat of reaction for the elemental volume in question. This tends to put limiting values on the temperature, but this limiting temperature is not simply $\frac{Q}{C}$ where C is the heat capacity of the elemental mass involved, because of the interplay of temperature dependence of reaction, and conductivity. This is discussed later (p 101).

Duhamel's Theorem

When the boundary conditions of a heat flow problem are time-dependent, the problem can be reduced to the corresponding problem with time-independent surface conditions by use of Duhamel's theorem. This method can also be extended to reduce the problem of a medium with time independent sources to the corresponding one with time independent source. This has been shown by Bartels and Churchill (3). The results of their work which are pertinent to heat flow problems are summarized in Carslaw and Jaeger (15), from which the following statement has been taken.

Consider the equation

$$\frac{\partial}{\partial x}\left(K_1\frac{\partial v}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_2\frac{\partial v}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_3\frac{\partial v}{\partial z}\right)+S(x,y,z,t)=\rho c\frac{\partial v}{\partial t} \qquad (5)$$

where, K_1, K_2, K_3 may be functions of x, y, z .

Let the boundary conditions be

$$k_1\frac{\partial v}{\partial x}+k_2\frac{\partial v}{\partial y}+k_3\frac{\partial v}{\partial z}+k_4 v = g(x,y,z,t)$$

where $k_1 \cdots\cdots k_4$ are functions of $x, y, z,$ only,

and let the initial condition be

$$\underset{t\to 0}{v}\longrightarrow \varphi(x,y,z)$$

Now if $F(x, y, z, \lambda, t)$ is the solution of the same problem except that $S(x, y, z, t)$ and $g(x, y, z, t)$ are replaced by $S(x, y, z, \lambda)$ and $g(x, y, z, \lambda)$, the values of these functions at time λ.

Then the solution of (5) is:

$$v = \frac{\partial}{\partial t} \int_0^t F(x, y, z, \lambda, t-\lambda)\, d\lambda$$

$$= \varphi(x, y, z) + \left[\int_0^t \frac{\partial}{\partial t}\left[F(x, y, z, \lambda, t-\lambda)\right] d\lambda\right]$$

E) <u>Regions with chemical sources</u> - As stated above, the problem of heat flow in a region containing chemical sources is not amenable to the ordinary methods of analysis. A general discussion of the problem of heat flow in a region containing sources is given by Carslaw and Jaeger (3). In this situation, there remains the following possibilities for obtaining useful information:

1. Limitation of the problem to certain specialized cases (e.g $\frac{\partial v}{\partial t} = 0$).
2. Approximation of the true form of the source by a form which is amenable to mathematical treatment.
3. Use ofcontinuous approximation methods (self-approximation).
4. Use of numerical methods (difference equations)
5. Use of analogue calculators.

Before proceeding with the above approaches, it will be useful to consider what information an intuitive analysis can give. The intuitive method would properly be included above, were it not such an integral part of every mathematical method. There is good basis for saying that every differential equation is solved intuitively.

Consider first the case of an infinite reactive medium, initially at some constant temperature v_0 , and in which a temperature pertubation is initiated at some point P (x,y,z). It is then obvious that, depending on the form and magnitude of the initial temperature pertubation, the heat of reaction of the material, the rate of reaction ofthe material, the conductivity, and the initial temperature, this pertubation will either be dissipated or will grow as time passes. The precise form expressing the relation of growth to the above parameters will be perhaps extremely complicated, but the qualitative situation is quite clear. The existence of a critical point is conditioned by the possibility of there being more heat generated in an elemental volume (per time interval) than can be conducted away. In the next time interval conditioned again by the degree of exhaustion of the reactive material, the high temperature coefficient of reaction rate will lead to even more heat being generated, and hence a spiralling of the temperature. As stated above, the maximum temperature will be largely a function of the initial temperature and the total heat reaction, but not entirely. Thus a region may be heated very rapidly so that reaction has not proceeded far by the time a high temperature is reached. Complete reaction without conduction would then lead to a somewhat higher temperature than simply calculated. Conservation of energy, of course, imposes limitations on the total heat for any region:

$$\int_{VOL} c\,(v - v_0)\, d\,VOL \leq \int_{VOL} Q\, d\,VOL$$

Where c is the heat capacity per unit volume of the material, v is the temperature, and Q is heat of reaction per unit volume.

The same factors are operative in a bounded medium, plus the additional effects of heat loss and addition over the boundaries, and the location of the initial pertubation with respect to these boundaries. Again, while the detailed interplay of the various effects arecomplicted, the general possibilities are clear. The important features for geology are that the amount of reaction, and the temperatures reached depend greatly on depth of burial, nature of initial material, heat flux from below, local mechanical or thermal stresses, and the like, which is certainly compatible with geologic experience. The geologic application of the scheme will be further discussed later (p. 140).

I. Special Cases of the Actual Problem

$$K \frac{\partial^2 v}{\partial x^2} + S = \rho c \frac{\partial v}{\partial t} \qquad (1)$$

1. **Assume** $\frac{\partial v}{\partial t} = 0$ for a certain time interval, and for all x.

For this to be possible, it must be assumed that $S \neq f(t)$ or, for a first-order reaction, since $S \propto \left(\frac{dm}{dt} = km\right)$ where k = specific rate constant, and m = no. moles reactant/vol., $m \neq f(t)$ and is, therefore, constant.

(In practice, this may not be too erroneous an assumption, as the reaction rate in solids will be largely diffusion controlled, and may not vary greatly with n. (see p.).

(1) then gives:

$$K \frac{\partial^2 v}{\partial x^2} + Rkm = 0$$

where R = heat of reactions in cal/gm. This may be written:

a. $$\frac{d^2 v}{dx^2} + \alpha e^{-B/v} = 0 , \quad \text{where } \alpha = \frac{Rm}{K} \qquad (2)$$

to solve, put $\frac{dv}{dx} = P$. Then

$$\frac{d^2 v}{dx^2} = \frac{dP}{dx} = \frac{dP}{dv} \cdot \frac{dv}{dx} = P \frac{dP}{dv}$$

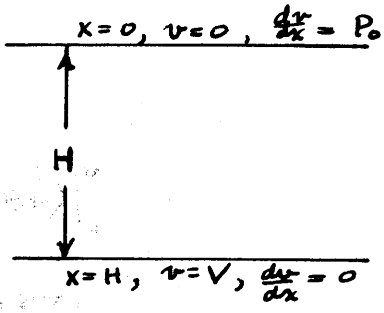
$$\text{and } \therefore \; P \frac{dP}{dv} = \frac{d}{dv}\left(\frac{P^2}{2}\right) = -\alpha e^{-B/v} \qquad (3)$$

Therefore, integrating,

$$\left|P^2\right|_{v=0}^{v=V} = -2\int_0^V \alpha e^{-B/v}\,dv \tag{4}$$

where V is the temperature where $\frac{dv}{dx} = 0$

whence (4) gives



$$-P_0^2 = -2\int_0^V \alpha e^{-B/v}\,dv$$

also from (3)

$$\left|P^2\right|_{P_0}^{P} = -2\int_0^v \alpha e^{-B/v}\,dv$$

therefore,

$$P^2 = P_0^2 - 2\int_0^v e^{-B/v}\,dv$$

$$= 2\int_v^V \alpha e^{-B/v}\,dv \tag{5}$$

whence

$$\frac{dv}{dx} = \sqrt{2\int_v^V \alpha e^{-B/v}\,dv}$$

($\frac{dv}{dx}$ is never negative, from the physics)

$$dx = \left[2\int_v^V \alpha e^{-B/v}\,dv\right]^{-1/2} dv$$

$$x = \frac{\sqrt{2}}{2}\int_0^v \left[\int_v^V \alpha e^{-B/v}\,dv\right]^{-1/2} dv \tag{6}$$

b. If S = constant, we have $\frac{d^2v}{dx^2}$ constant = B, say. Then $v = -\frac{1}{2}Bx^2 + BHx$, after using boundary conditions of a.

c. If $S = A - \frac{A}{1+Bv}$

(3) above gives

$$\frac{d}{dv}\left(\frac{p^2}{2}\right) = A - \frac{A}{1+Bv}$$

$$P - P_o^2 = 2A\left|v - \frac{1}{B}\ln(1+Bv)\right|_0^v$$

$$= 2Av - 2A/B\ \ln(1+Bv)$$

that is,

$$\left(\frac{dv}{dx}\right)^2 = 2A\left[v - \ln(1+Bv)^{1/B}\right] + P_o^2 \qquad (8)$$

Which must be integrated numerically, but involves one less integration than (6).

The significance of (6), (7), and (8) is that they define a curve $v = f(x)$ for every value of H taken. Then if at any point in a given mass with this temperature distribution, v is increased, equilibrium will be disrupted, and (without assumptions $S \neq f(t)$) , spiralling of temperature will result.

Geologically, the results could be used to give an approximation of the maximum depth of sediment that would not "autocatalyze".

Other boundary conditions can be treated, such as $\left(\frac{dv}{dx}\right)_X$ = constant.

2. Consider an infinite reactive medium initially at v = 0, in which a temperature disturbance, as a sort of thermal tide, has been preceeding for a long time. Then, assuming an equilibrium "phase" velocity of the front has been reached, (which equilibrium velocity is suggested both intuitively and from measurements of gaseous explosions.

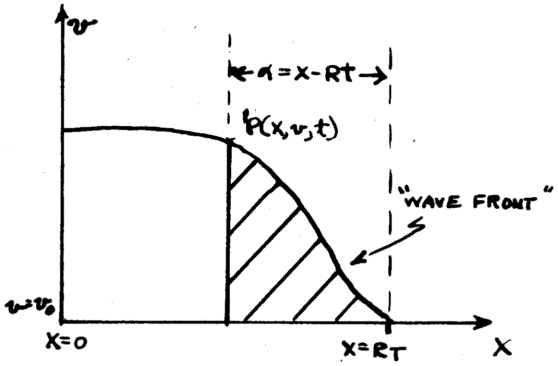
We have $\left(\frac{dx}{dt}\right)_v$ = constant = R, say.

Now $dv = \left(\frac{dv}{dx}\right)dx + \left(\frac{\partial v}{\partial t}\right)dt$, always

therefore THE ABOVE gives

$$\left(\frac{dx}{dt}\right)_v = -\frac{\left(\frac{\partial v}{\partial t}\right)_x}{\left(\frac{\partial v}{\partial x}\right)_t}$$

$$=' R$$



and $$-\left(\frac{\partial v}{\partial t}\right)_x = R\left(\frac{\partial v}{\partial x}\right)_t \quad (1)$$

Then substitution in

$$K\frac{\partial^2 v}{\partial x^2} + S = \rho c\frac{\partial v}{\partial t}$$

gives
$$K \frac{\partial^2 v}{\partial x^2} + S + R\rho c \frac{\partial v}{\partial x} = 0 \qquad (2)$$

Now (1) is obviously satisfied by v = f (x-Rt) = f(α) say, where the significance of α is shown in the sketch, the time and space origins being related by x = 0 = t for v = 0.

With regard to S , if H = heat of reaction / unit volume,

$$S = HA e^{-B/v} e^{A\int_0^t e^{-B/v} dt} = H \frac{dm}{dt} = H k m$$

and the integral $\int_0^t e^{-B/v}$, which expresses the decrease in amount of reactant, obviously depends only on α . This is obvious from the figure, since v = 0 for x = 0, t = 0 and can also be seen since $\frac{\partial \alpha}{\partial t}$ = - R.

Therefore,

$$\int_0^t e^{-B/v} dt = \int_{t=0}^{t=t} e^{-B/v}\left(-\frac{d\alpha}{R}\right) = -\frac{1}{R}\int_0^{\alpha} e^{-B/v} d\alpha$$

Whence (2) can be written

$$K \frac{d^2 v}{d\alpha^2} + R\rho c \frac{dv}{d\alpha} + S(\alpha) = 0 \; ,$$

which is now an ordinary differential equation.

The solution of this equation would yield data on the relation of width of contact (as for a growing porphyroblast) to rate of growth, and the parameters K, ρ, c, H, A, B.

Solution of this would have to be achieved numerically, or perhaps some algebraic transformation would simplify it.

Boundary conditions are:

$$v = v_0 , \quad \text{for} \quad \alpha = 0 \; ;$$

$$\begin{cases} \frac{dv}{dx} \to 0 , & \text{for} \quad \alpha \to -\infty \\ \text{or } v \to \text{constant} & \text{" \quad " \quad "} \end{cases}$$

An approximation to the true source can be made by assuming that the amount of reactant consumed is proportional to the temperature. Then if V is the final temperature, the amount remaining M(V–v) where M is a constant which can be determined from existing parameters.

Then assume rate $\propto v(V-v)$

or $\propto e^{-B/v}(V-v)$

etc.

3. Consider a single cell of homogeneous temperature, with heat loss over one or both boundaries.

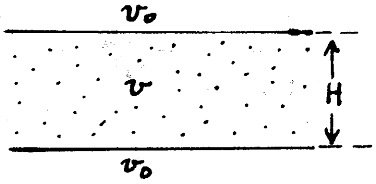
a. Radiation into medium at constant temperature

Equation is

$$\rho c \frac{\partial v}{\partial t} = S - 2k(v - v_0) \qquad (1)$$

where k is the radiation constant

(a)

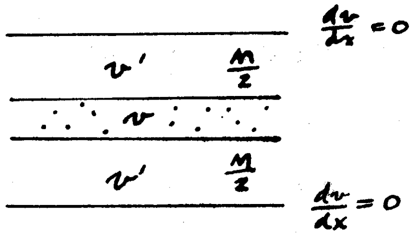


b. Radiation into well-stirred fluid of mass M, specific heat λ temperature $v'(t)$ initial temperature. v_0 .

At any time

$$v' = \frac{1}{M\lambda}\int_0^t k(v-v')\,dt$$

(b)



and equation is

$$\rho c\frac{\partial v}{\partial t} = S - k(v-v')$$

$$= S - k\left[v - \frac{1}{M\lambda}\int_0^t k(v-v')\,dt\right.$$

Which could be solved by continuous approximation, or by step-by-step integration.

Cases such as the above, correspond to the geological case of reactive strata between inert ones. Other boundary conditions, and ones of the most complicated time-dependence, could be used above easily.

a. (1) has critical point for constant amount of reactant when

$$\frac{dv}{dt} = 0 \;; \qquad i.e. \quad S = 2k(v-v_0)$$

for mass constant, this is

$$Ae^{-B/v}\,1\,.\,m = 2k(v-v_0). \qquad \text{where } m = \text{mass/vol}$$

therefore, for k large, v can be large;
for A large, v cannot be large;
for B small, v cannot be large;
if $\frac{dv}{dt} = 0$; $m =$ constant.

etc... , all of which is obvious, and checks with earlier conclusions.

II. Approximation of S by a More Tractable Form

The essential feature of the chemical source is that it is temperature dependent, and that

$$\int_0^\infty S\,dt \leq n_o H \quad \text{for all } x$$

when n_o = no. moles/vol

H = heat reaction/mol

S may be approximated by forms which at least do not integrate to infinity. i.e.

$$\text{(i)} \quad S = A e^{-B/v} e^{-\lambda t}$$

$$\text{(ii)} \quad S = A v e^{-\lambda t}$$

$$\text{(iii)} \quad S = A v e^{-f(t)},$$

or in general, $\text{(iv)}\ S = f(v)\, g(t)$

These are not completely satisfactory, since the factor decreasing S should have a position dependence. If it does not, then in a medium in which a disturbance has propagated a "source" can die down to zero without there having been any reaction. This would preclude the continuation of thermal catalysis in time.

Solution of all but (ii) above can only be achieved by step-by-step integration, continuous approximation, or some analogous calculatory device.

The solution of (ii) is possible, and is given on the following pages.

(Note that Duhamel's theorem cannot handle these cases because v in the source includes t.)

(ii) Approximating true form of S.

Let $S = f(x,y,z,t) + v \cdot g(t)$

then equation (I1) is

$$K\nabla^2 v + f + v \cdot g = \rho c \frac{\partial v}{\partial t} \qquad (1)$$

Now substitute

$$v = \theta e^{\int_0^t g/\rho c \, dt}$$

i.e.

$$\frac{\partial v}{\partial t} = v \cdot g/\rho c + \frac{\partial \theta}{\partial t} e^{\int_0^t g/\rho c \, dt}$$

$$\text{and} \quad \nabla^2 v = \nabla^2 \theta \, e^{\int_0^t g/\rho c \, dt} \qquad (2)$$

which gives

$$K\nabla^2 \theta e^{\int_0^t g/\rho c \, dt} + f + v/g = v/g + \frac{\partial \theta}{\partial t} e^{\int_0^t g/\rho c \, dt}$$

Cancelling the v/g terms, and factoring out the common term $e^{\int_0^t g/\rho c \, dt}$, (which is never zero,)

$$K\nabla^2 \theta + f\left(e^{-\int_0^t g \, dt}\right) = \frac{\partial \theta}{\partial t} \qquad (3)$$

that is, the equation has been reduced to a solvable form, since $f = f(x,y,z,t)$ only. This solution has been adapted from that given by Paterson (79).

Forms for $g(t)$

A) The simplest form of the desired sort (i.e. for which $\int_0^\infty g\,dt$ is finite) is $g = e^{-\lambda t}$

then $\int_0^t g\,dt = -\frac{1}{\lambda}\left|e^{-\lambda t}\right|_0^t$

$$= \frac{1}{\lambda}\left(1 - e^{-\lambda t}\right)$$

and from (2)

$$v = \theta e^{\frac{1}{\lambda \rho c}\left(1 - e^{-\lambda t}\right)} \qquad (4)$$

From an inspection of (4), it is obvious that the term $e^{\frac{1}{\lambda \rho c}\left(1 - e^{-\lambda t}\right)}$ is the thermal catalysis term, as is seen from putting $t = \infty$, which reduces v to the form of θ.

This term has the form which was deduced intuitively, i.e. for small ρc, that is, when a small amount of heat is required to cause a large variation in temperature, the term is large. Also, if λ is small, that is, if the reaction occurs very rapidly, the effect is large. This is at least so for small t.

However, it is obvious that the form $e^{-\lambda t}$ is only a rough approximation, and a term including v should be used.

Concerning boundary conditions, θ will have the same boundary conditions as v, if they are of the form $v = 0$, $\frac{dv}{dx} = 0$, for certain x, and all values of t.

Finally, note that the approximation $S = v \cdot g(t)$ is very seriously lacking, in that the $g(t)$, which takes account of the disappearance of the reactant, does not include a space term.

3. a. The only semi-analytic method which is applicable to an arbitrary temperature-dependent source is that of continuous approximation (sometimes called self-approximation). This method of attack is very frequently used in physics, notably in Hartree's self-consistent field approximation for atomic wave functions.

The method is as follows:

Consider the equation: $K \frac{\partial^2 v}{\partial x^2} + S = \rho c \frac{\partial v}{\partial t}$,

where $$S = A e^{-B/v} e^{A\int_0^t e^{-B/v} dt}$$

Then if we estimate the solution, that is, if we put $v = V^\circ$, where V° is some function of x, t substitution in (1) gives

$$K \frac{\partial^2 v}{\partial x^2} + S(x,t) = \rho c \frac{\partial v}{\partial t}$$

In this equation, **S** is now a function of **x** and **t** only. It can therefore be solved, in theory, using one of the following:

a. Integral transform methods.
b. Green's method - integration of source solutions.
c. Computing devices.

The result of these methods will then give a solution

$$v = V'(x,t) \text{ , say.}$$

This is then re-substituted in (1), and the cycle repeated until the successive values of v converge. If a poor initial guess for V^0 is made, the values may be slow in converging. However, if some other method, as a step-by-step calculation, is used to suggest this initial form, the work is not generally excessively laborious, The step-by-step method is explained below.

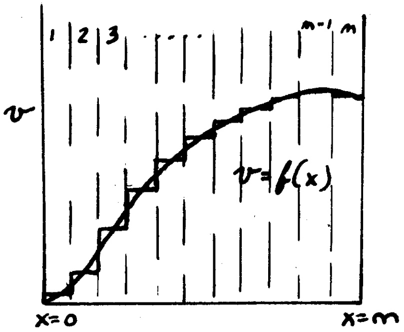
4. Numerical Calculation

a. Step-by-step method. Step-by-step integration is the most brutal method of attack on the problem, but also the most sure.

The procedure is to form cells in space and time, and follow the changes through in a step-by-step fashion. Thus, if we have for the problem that

$$\underset{t \to 0}{v \to f(x)} \qquad \text{and} \qquad \left.\begin{array}{ll} v = 0 & \text{for } x = 0 \\ v = V & \text{"} \quad x = m \end{array}\right\} \text{for all } t$$

then $f(x)$ is approximated as in the sketch. This is then the temperature distribution at time t = 0, and the temperature is therefore known for each of the cells 1, 2, ... m Now, assuming no reaction, the temperature distribution at some later time $t = t'$ is calculated. Next, assuming no conduction, the temperature $f'(x)$ after the interval as a result of reaction is calculated, using for the initial



temperature the distribution $f'(x)$ just calculated. The process is then repeated for a second time interval, and so on. The results can be made more exact by reversing the order of steps above: that is, by assuming the temperature is modified by reaction, each cell acting adiabatically, and then assuming conduction modified this, with no reaction.

This method can be made as accurate as one chooses, by increasing thenumber of time and space cells. The only limit is the amount of labour which can be expended. The time and space cells do not necessarily have to be kept constant in size - where the function is found to be slowly varying, large cells can be used.

In summary of the above methods , it is important to note that neither 3 nor 4 can give an analytic form for v. Thus, critical points must be determined by comparison of results, for different parameters. One "run" will not give them. This fact is unfortunate for the geologic case, in which parameters are poorly known. It would be of course much more useful to be able to fit an analytic result to the observed field facts, and determine the values necessary for the parameters.

5. Analogue Calculators.

a. Adaption of the problem to solution by commercial calculating machines depends on the machine to be used, and therefore does not fall into the field of the present work.

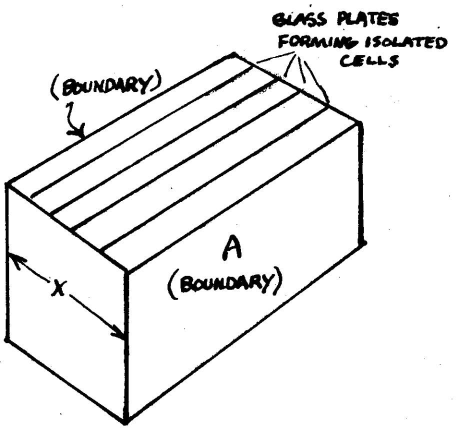
b. More specialized analogues for the problem may be devised as:

(i) Electrical models
(ii) Mechanical models
(iii) Chemical models

(i) A condenser-resistance-inductance device to solve the diffusion equation has been constructed at Columbia University. This is not at present adapted to work on problems involving sources, but could be so adapted. Treatment of very complicated sources would probably be impossible on this particular device, however.

(ii) It is not difficult to devise mechanical models which can be used to calculate all or part of certain problems. The writer has devised one such instrument, but as there is no real difficulty to such endeavours, it will not be described here.

(iii) The most obvious type of model to use is a chemical model. Actually, such artificial structures as dams may be thought of as models of geologic situations. A true scale model would probably be impossible, though the writer has not investigated this fact. The chief drawback for quantiative work is the difficulty in obtaining sufficiently good data on the kinetics of the material used. The problem will not be discussed further here. However, a sketch of a model which could give a qualitative results is appended.



The sketch shows a rectangular box which represents the system to be studied. The box is separated into longitudinal segments by spacers of glass or other material. Each segment represents a space cell of the type used in section above, as is indicated on the diagram.

The side A of the box, and the side opposite to it correspond to the upper and lower boundary of the medium studies, and boundrary conditions are applied directly. Each cell is filled with a fluid in which takes place some reaction. Thekinetics and heat effects of this can be determined directly in the above set-up.

To employ the device, initial conditions of the problem are modelled by varying the amount of reactants present in each cell, and the temperature of each cell. The latter can be done by pre-heating, or using individual heating coils.

It is not proposed to discuss this model at length. There are a number of obvious difficulties and advantages. Difficulties are chiefly centered around mechanical heat losses. These losses could be partly accounted for by direct measurement on themodel. The main advantage of the model is that the rather complicated temperature-mass dependence of the reaction rate is immediately approximated. Also, a large variety of initial and boundary conditions, and a large range of values for the parameters, can be readily accomadated.

F. Discussion and Approximate values.

In the preceeding sections, various methods of attacking the mathematical aspect of the problem have been indicated. It has been shown that there is no simple method of obtaining analytical solutions of the problem. In the present state of knowledge of geologic reaction rates and heats it is of little significance to carry through any of the numerical methods suggested. This is certainly so for the purpose of the present paper, which is as intended as an outline of the general problem. (For particular cases, calculation is, of course, useful and highly desirable.

In this situation, the most obvious question is whether thermal catalysis is likely to occur at all. If the geologic values are such as to make this phenomenon impossible, then the general hypothesis assumes a nebulous tinge, to say the least. In the following, rough calculations are made of the temperature at which reaction heat would equal the heat conducted away, assuming the terrestrial heat flow to be one michrocalorie per square centimeter per second.

For any given cubic centimeter of rock, per unit time, there will be an amount of heat flowing in from below, and another mount flowing out at the top. It is assumed there is no flaw out of the sides. If there are no sources, and there is equilibrium, then these heat flows are the same. Here, it is proposed to neglect the incoming heat and demand that reaction proceed rapidly enough to equal the observed outward flow. This is then an extreme case-actually, there is much evidence that the thermal gradient of the earth flattens with increasing depth. Also, local gradient reversals are neither impossible nor unknown. A more accurate method would be to use the method of Part E.1. However, the present method is not incompatible with the accuracy of the reaction-rate data. The reaction rates used are those given in section VB. The results are given in Table XII. The temperature given is the temperature at which the reaction head would just equal the heat removed. Increase in temperature would then lead to thermal catalysis (but see also section VIe.

TABLE XII

TEMPERATURE AT WHICH REACTION HEAT/CM^3 EQUALS TERRESTRIAL HEAT FLOW/CM^2

Reaction No (pages 87-90)	Reference	$-\Delta H$ in kcal/mole	q kcal/mole	T deg. C
4	Jagitsch	10.	112.	1100.
8	Segawa	"	75.	520.
11	Table XI	"	40.	320.
14	"	"	60.	200.
17	"	"	80.	165.
20	"	"	100.	140.
21.	"	"	100	75.

As a <u>sample</u> <u>calculation</u>, we use the results of Jagitsch (49), already listed. For the reaction $MgO + MgSiO_3$, he gives $\frac{dm}{dt} = 1 \times 10^5 e^{\frac{-112000}{RT}}$ in moles per square centimeter of contact per second. Because of ignorance of the area of contact, this is difficult to apply geologically. However, it is only desired to indicate the general method.

The following assumptions are made:

a. The heat of reaction is 10,000 cal/mole = 10^4 cal/mole

b. The density of the material is 3 gms/cm^3

c. The surface area is 3 square meters per gram (see page 75)

Then per cm^3, the heat produced per second is

$$\frac{d\,(\text{Heat})}{dt} = (10^{4})\left(\frac{3\times10^{2}}{3}\right)(10^{5})\, e^{\frac{-112{,}000}{RT}}$$

$$\doteq 10^{11}\, e^{\frac{-56{,}000}{RT}} \quad \text{calories/second/cm}^3$$

Now if

$$10^{11}\, e^{\frac{-56{,}000}{T}} = 1\times10^{-6} \quad \text{cal/cm}^2\text{/sec (the normal heat flow)}$$

$$e^{-\frac{56{,}000}{T}} = 10^{-17}$$

$$10^{\frac{-23{,}000}{T}} = 10^{-17}$$

$$\therefore\ T = 1360^\circ K$$

$$\doteq 1100^\circ C.$$

In such calculations, the most critical value is that of the activation energy. Above, if the activation energy were 60 kilocalories per mole, as it is for some of the other reactions listed by Jagitsch-see page 87 - the above critical temperature would be only 490 C.

The results of the above table show that, from values that are available, thermal catalysis is a definite possibility. Comparison with the other reactions of Segawa, given in Section VB, shows that the rate used may be low. The results are reasonable, in that reaction heat is not generated so rapidly as to make thermal catalysis a certainty once sediments are compacted. If the values did suggest that this thermal catalysis is inevitable for every sediment, an error would of course be indicated, since this is contrary to geologic evidence, (see e. g. Lyons (67)). The point of importance is that, with not-unreasonable assumptions, the phenomenon could occur.

Another indication of the effect of activation energy may be given as follows. Suppose we consider the first-order reaction $\frac{dm}{dt} = -km$. Assuming constant temperature and integrating, we have $\frac{m}{m_0} = e^{-kt}$, where m_0 is the number of moles at time $t = 0$.

Also, suppose that k is of the usual form $k = C e^{-\mathcal{E}/RT}$. Then, if we assume that there are certain pre-Cambrian rocks only 10% reacted", and certain Tertiary rocks 90% reacted, it is interesting to calculate what the parameters would have to be to accomodate this fact. This is easily done, with the following results:

1. Assuming the activation energy is 100,000 calories per mole.

If the average temperature of the pre-Cambrian rocks was 127° C, the temperature of the Tertiary rocks would have to have been 150°C.

If the temperature of the pre-Cambrian rocks was 227°C, the corresponding Tertiary temperature would have to have been 262° C.

2. Assuming the activations temperature 50,000 calories per mole.

For average Pre-Cambrian temperature 127°C, the average Tertiary temperature would be 173°C.

For average Pre-Cambrian temperature 227°C, the average Tertiary temperature would be 300°C.

From the above it is seen that it is not difficult to reconcile the geologic occurence of Tertiary granitization and un-granitized Pre-Cambrian material. The length of time to the early Pre-Cambrian is only about thirty times that to the early Tertiary.Rather slight variations in activation energy and temperature can then affect resolts greatly.

VIII. GEOLOGIC IMPLICATIONS

The implications which existence of potent chemical heat sources would have for geology are far-reaching. Some of these have been indicated in the preceding pages, and others cannot be easily discussed because of lack of quantitative information. The following is intended to indicate the general fields in which the chemical factor would be relevant, and to point up the situation with geological examples.

For ease of treatment, the points to be considered may be grouped roughly according as they are related either to terrestrial heat flow, or to metamorphism.

a. Terrestrial Heat Flow.

1. General precise data on the nature of terrestrial heat flow would provide a check of existing theories of large scale earth processes, and might suggest new ones. Measurements have been increasing in number and quality, but have been under way for little more than a decade. Demonstration of the efficacy of chemical sources and sinks in the cruse must cast extreme doubt on the significance of heat flows values deduced without consideration of the chemical factor.

As a corallary, theories regarding crustal structure, age of earth, interior structure and the like, which are based upon heat flow measurements, must be critically examined. It is not necessary, of course, that all measured values should be significantly wrong - some regions are effectively inert, and in others no significant reactions have occurred.

Recognition of the importance of chemical energy in such problems would constitute, in a sense, a triumph for geology, in that it would underline the necessity of considering the masses in question as geological bodies. Rocks are not inert media, with definite, simple, thermal and mechanical properties, but are in a sense living and mobile. Each part of a rock reacts according to its own past history, nature, and environment, and the influence of these characteristically geological factors cannot be disregarded.

There is a certain analogy between the frequent neglect of this geologic factor in many "exact" treatments ("approximate" is more nearly correct) and Kelvin's neglect, or rather ignorance, of radioactivity in deducing his geologically untenable results (56). Similarily, Huxley's dictum on the "mathematical Mill" has lost none of its appropriateness today, when "exact" deductions regarding geology are becoming increasingly common. The quotation in mind is:

"But I desire to point out to you that this seems to be one of the many cases in which the admitted accuracy of mathematical processes is allowed to throw a wholly inadmissible appearance of authority over the results obtained by them. Mathematics may be compared to a mill of exquisite workmanship, which grinds you stuff of any degree of fineness; but, nevertheless, what you get out depends on what you put in; and as the grandest mill in the world will not extract wheat-flour from peascods, so pages of formulae will not get a definite answer out of loose data".

As one alteration, "loose assumptions" might better be used than "loose data".

2. Mathematical Relations.

Heat flow values are determined from a combination of depth-temperature and depth-conductivity logs. The principle is clear from a consideration of the fundamental equation

$$K \frac{\partial^2 v}{\partial x^2} + S = \rho c \frac{\partial v}{\partial t} \qquad \text{———} \quad (1)$$

or

$$\frac{\partial}{\partial x}\left(K \frac{\partial v}{\partial x}\right) = \rho c \frac{\partial v}{\partial t} - S$$

Thus, if equilibrium has been established, and if there are no sources, then

$$\frac{\partial}{\partial x}\left(K\frac{\partial v}{\partial x}\right) = 0$$

and the heat flow $\left(K\frac{\partial v}{\partial x}\right)$ is constant with depth. It can therefore be determined by averaging values obtained for short segments, and the assumptions can be checked with the resultant depth-heat flow curve. Inconstancy with depth has been noted in a number of occurrences. Close to the surface, these variations have been attributed locally to the lingering effects of Pleistocene glaciation. Otherwise, variations in the conductivity in situ from that measured in the laboratory have been appealed to. In at least two cases of heat flow measurement, however, another factor has had to be suggested. These cases have been described by Bullard (14A) and in each, he has attributed the distrubance to water flowing in sedimentary beds. Water, oil and gas are definitely known to have caused sharp local thermal effects in strata, but with respect to the cases mentioned, there are other possibilities. This will be discussed further in the next section.

Theoretically, depth-temperature conductivity logs offer an ideal means of empirically investigation the equation (1). With assumptions as to the nature of $\frac{\partial v}{\partial t}$, it might be possible to obtain data concerning the parameter's in S. In practice, a difficulty would be the determination of the conductivity of the rocks in situ sufficiently accurately. For the present purpose, it is sufficient to point out the variations that have been observed, and their possible origin.

c. Local geology and heat flow.

There has been for some time a recognition of the relation of heat flow, or rather thermal gradient, to underlying structure in sedimentary rocks. This situation has been discussed by Thom (113A,B) and by Van Orstrand (117). There is a definite tendency for high thermal gradients to be found over anticlines, and low gradients over synclines. In many cases, suitable plots of thermal gradients mirror closely the true contours of the structures drilled. For example see the references cited.

More recently, Bullard and Niblett(14B) have published information on certain anomalously high heat flow values in Yorkshire, England. The bores investigated show heat flows of up to 2.8 microcalories/cm.^{2}/ sec., compared to an accepted "normal" value of 1. The high values are explained by ground water heated at depth, flowing up through the porous strata. It is shown that, with certain assumptions regarding temperature, a rather moderate seepage would be required to give the observed results. However, the hydrodynamics of the situation is purely hypothetical, and in particular, fails to explain why the higher heat flow is not on the anticlinal flank, rather than at its crest.

For reasons of space, the paper cannot be discussed completely. It is, however, submitted that this case is related to the structure-gradient tie-up just mentioned. In these earlier cases, heat flow was not computed, but would parallel the gradients, in general. It is also interesting to note that water flow in strata has been suggested to explain these situations also. The arguments in favor of this explanation have not been strong -- See the letters of Thom (113B) and Washburne (119).

The thermal gradients have been otherwise explained as due to uplift of strata formerly buried at higher temperature levels. It isreported by Thom (113B) that Van Orstrand computed that at a depth of two miles, 22percent of any original temperature variation would remain after 100 million years.

If exothermic reactions were assumed in the concerned, the facts would be rather readily explained. Chemical differences in beds would cause the temperature to reflect the structure, and temperature excesses could persist for much longer times than in the case of inert strata. Which of the two explanations is the more correct could probably be evaluated by detailed study of the gradients. For inert masses, temperatures in nearby beds of different composition would tend to be identical, while large temperature difference might occur if reactions proceeded.

In the opinion of the writer, uplift of inert strat from deep zones does not seem quantitatively capable of explaining the rather sharp structural delineations observed.

High and erratic thermal gradients flowhave also been reported to occur in the lava fields of Oregon and Washington by

Hot springs provide striking examples of local temperature variations. It is not possible to give detailed instances, because of space, but it is again so that no completely accepable explanation for such springs has been forthcoming. For discussion ofthe various theories, see reference (128). Exothermic reactions in the rocks concerned is again a possibility. For such hot spring areas as those of Arkansas (described by Bryan in the above reference), where there is very great lateral extent, and no evidence of underlying igneous intrusion, chemical reaction should be particulary considered.

In these cases, the source of the water as well as the source of the heat has not been satisfactorily explained. In the case of chemical energy such water may be connate water and structural water, driven off by the reactions.

Regional and large scale geology

As regards regional temperatures, the data of Van Orstrand (117) shows that the thermal gradients in ancient crystalline areas, as Northern Ontario and Northern Michigan, are low relative to those in sedimentary areas. Since the average conductivity of sediments is higher than that of the crystallines, thisiimplies a higher heat flow in them.

Study of heat flow over broad areas, with the object of determining primary flow, would lead to additional data on the state of the mantle and core.

The writer is aware of only one reasonably accurate gradient measurement on the sea floor. This was obtained by the recent Swedish expedition, and gives a very high value for the heat flow. Before any profound deductions regarding crystal structure are based upon such measurements, it must be certain that the effects of exothermic and endothermic reactions can be neglected.

Effects of heat produced in the crust would effect not only the overlying areas, but might provide sufficient temperature perturbation in the upper mantle to initiate convection. For examples of the effect of surface temperature perturbation on convection see Pekeris (80).

With regard to convection in the mantle, reactions in the mantle itself might be of extreme importance. This possibility can at present only be noted, since there is no data on such reactions. A useful investigation, however, would be to study the transition heats determined by Bridgman (10B) in an attempt to estimate the order of magnitude of the effects likely.

b. Metamorphism

Metamorphism is characterized by the occurrence of transformations of the sort included in this paper as chemical, and there is therefore no doubt that heat effects accompany metamorphism. There is a rmote possibility that, over some region, endothermic effects will balance endothermic effects, with no resultant change. However, that this situation should be so at each point is not conceivable. In the following sections, some aspects of metamorphism relative to the problem are discussed.

1. Diagnetic processes.

There is no fundamental difference between the nature of the changes occurring in diagenesis and those of metamorphism as usually considered. Changes in sediments occur as soon as they are deposited, as has been well established by many authors e.g. Leith (63) The mechanism of many of the processes, as dehydration, recrystallization, authigenic growth, ion absorption and the like, are still imperfectly understood, but again the point is that they have occurred, and that there is some heat effect. There seems to be enough data already available, particularly as regards to dehydration, for some preliminary magnitudes to be stimated, but this has not been done here.

As has been mentioned earlier, the near-surface diagnetic environment is one in which the general mobility leads to the possibility of rather rapid processes — both as regards reaction and heat dissipation. The net effect is then by no means easily predictable. There has been very little study of the depth temperature relation in this environment. One rather high value of the gradient, obtained by the recent Swedish expedition (129), is suggestive of reactions, if high heat flow over the ocean floor is not assumed.

Already mentioned (p.36) is the point that the more completely equilibrium is established in this region of efficient heat removal, the less possibility there is of burying a chemical energy source.

Finally, attention is called to the relation of simple transformations such as calcite -aragonite, and gypsum-anhydrite.

These processes are often easily followed, and since the mechanism is similar if not identical to that of more extreme metamorphic transformations, they are instructive.

In recent years, an increasing number of minerals has been shown to occur authigenically. Among these are garnet, staurolite, brookite, and others frequently regarded as being native to higher temperature environments. Such facts are not easily reconciled with the point of view that the appearance of so-called index minerals in metamorphic stages reflects changes in thermodynamic equilibria. The facts are, however, readily explicable on the basis of the rate.

[CONTINUED ON NEXT PAGE]

effect. (p. 35).

To conclude, it is important to recognize that the minerals of authigenesis are in many, if not all, cases, valid "rock-making" minerals, and not mere accessories. The extreme cases are of course quartz and feldspar. For each of these, there is often the difficulty distinguishing the secondary from the primary species, a difficulty which of course does not occur with respect to the less ubiquitous minerals. For this reason, while the literature is replete with descriptions of authigenic feldspar, the occurrences described are usually in limestone of sandstone, where there is little or no clastic feldspar. However, at least two occurrences of feldspare in shaly material have been discussed. The workers in question have been Gruner and Thiel (41) and Moore (74).

Gruner and Thiel worked with samples of the Glenwood and Decorah shales (41) and with shaly beds in nearby dolomite. After solution of the calcite cement, size analysis showed two distribution maxima - a large on (48%) at 1/16mm and a smaller one at 1/ 512 mm. Investigation of the finer fractions showed it to be mostly orthoclase with no X-ray evidence of quartz, mica, or kaolinite. The larger fraction was mostly quartz. Details are to be found in the above paper, but the essential argument of the authors is that the fineness and homogeneith of the fine fraction rules out a clastic origin. One would not expect such a sharp division of orthoclase and quartz in normal erosion. One would not expect such a sharp division of orthoclase and quartz. There is stated to be no evidence of hydrothermal activity in the area, or of mineralization. Neither is there evidence of deep burial of the material.

Moore reports the occurence of authigenic albite in the Green River formation, which is a Middle Eocene marlstone with dolomite the dominant mineral. Albite occurs in rhombs of maximum length of 3 millimeters. The feldspar is confined to members of the formation with high organic content. Moore's conclusions are that the albite is unquestionable authigenic, and that it necessarily formed at low temperature.

Numerous references on authigenic feldspar are given by Boswell (9), Tester and Atwater (112), and in reference . A description of feldspar replacing fossils is given by Stringham (104).

Philosophically, there can be no objection to the occurrence of authigenic feldspar in shale. Clearly, there is more material of the proper compostion available in such material, and it would be surprising if it were absent. The small size of the feldspar in the case reported by Gruner and Thiel may be analogous to the small size of devitrification crystllites in glass at low temperature mentioned on page . In such cases there is a large number of nucleation centers, but growth of individual centers is retarded.

Until some simple criteria are established for distinguish -

ing the authigenic feldspar, it is interesting to speculate as to what amount of the feldspar and quartz in Pre-Cambrian arkose is authigenic. It is conceivable that the prevalence of such rock types in the pre-Cambrian is partly explicable on the basis of authigenic growth. It is of course, so that many of the feldspathic rocks in question show clear lithologic evidence of rapid deposition - that is, cross-bedding, graded bedding, and the like. Thus the stated hypothesis, in these cases at least, can be only a side-effect. Otherwise, the situation may be analogous to the lack of aragonite in ancient sediments. This lack is apparently not due to an essential difference in the ancient depositional environment, but to the sluggish aragonite-calcite inversion.

2. Metasomatism in metamorphism..

The subject of metasnomat is intimately connected with that of metamorphism, and must therefore be discussed on this basis. Moreover, it is of fundamental thermodynamical importance to know whether the metamorphic system being considered is open or closed, as has already been indicated (p. 59).

Briefly, the point to be emphasized here is that, while there is often no doubt of the removal and addition of material in metamorphism - as in dehydration of sediments, in silicification and mineralization adjacent to veins, and in other obvious cases, many metamorphic systems have been, or better, could have been, closed.

There is a good deal of indirect geologic evidence on this point. Examples of short-range diffusion of the order of centimeters are very numerous and frequently very striking. These are common, and have so frequently been described in the literature, as to make further mention here unnecessary. On the other hand, it is difficult to find direct evidence of long distance addition of removal of material throughout gelogic volumes. Commonly, such cases are based upon deductions from chemical analyses, and it is submitted here that many such deductions have little validity.

For example, it is common to discuss the metasomatism involved in metamorphism by comparing analyses of the metamorphic rock with analyses of the "average rock" of the type assumed to be the parent, or with analyses of the rock from less metamorphosed zones. The main objection to this is that the "average rock" analysis, particularly where pelitic sediments are concerned, is usually quite useless as an indication of the precise composition of any one aspect. Again, within any one sedimentary member, there is well-substantiated evidence of initial sedimentary variation in composition. Even in deep-water clay (5000 meters) such a variation occurs, and equilibrium would be more closely approached in such bodies.

Thus in a clay from 5000 meters, cored off Bermuda, Na_2O Varied from 2.4 % to 3.9 %, K_2O from 2.9% to 2.4 %, and the Na_2O/K_2O ratio from 0.9 % to 1.6%. The core was 35 meters long. This data was kindly supplied by Professor Ahrens, from analyses in his possession.

The factor of "sedimentary differentiation" has been discussed recently by Kennedy (<u>57</u>). The Moine Schists of the Northern and Central Highlands are not generally considered to be the metamorphosed equivalent of the Torridonian formation. This latter is, however, characterized by less silica, more alumina, and higher soda-potash ratio. Following certain earlier workers, Kennedy suggests that these differences may be due to original differences in the sedimentation. There is supporting evidence of a similar sedimentary differentiation across the Caledonian syncline in the Sulitelma area of Norway, described by Vogt (118A). These rocks are unmetamorphosed, and Vogt explained the differences as being due to variation in " residual" character of the sediments. However, in explaining a closely similar chemical variation in the metamorphic sparagmite rocks of the Norwegian Caledonian geosyncline, Barth (4A) has appealed to progressive metasomatism. In view of the evidence cited above, and the more complete review of Kennedy, there may be no basis for such a theory. Such metasomatism is moreover extremely difficult to visualize.

Similar doubts beset deductions of the type made by Lapadu-Hargues (61). From average analyses of shales, slates, phyllites, gneiss and granite, he demonstrates striking variations in some elements, particularly soda. However, granting the reality of the variation, it is not necessary that it should be correlated with the mechanism of metamorphism. The soda content is seen to increase with metamorphism, but metamorphism and soda content may be each the result of some other process, and bear no genetic relation one to the other.

The true nature of the processes controlling such original differences in sediments and other rocks is undoubtedly complex, and no detailed discussion can be given here. It is desirable, however, to point out the role which rate of deposition may play.

There are at least three ways in which this factor may have an effect. Sodium and Potassium are here used as examples. First, rate of erosion and therefore deposition may be correlated with a less "residual character" of the material. In other words, high rate of erosion would tend to approach mere mechanical fractionation of material, of the type of postulated for arkose formation.

Second, there may be mechanical entrapment of sea water with rapid burial, from which connate water soda might then be extracted by various reactions.

Third, there is the effect of ion absorption on the clay surface. It is unlikely that, even if complete equilibrium of the clay particle with respect to ion exchange at the surface is established during transport, it will be in equilibrium when in the locale of deposition. Depending, then, on the rates of the equilibrium reactions, there will be a process of ion exhchange on the sea floor. A close examination of known depositional rates and sea floor chemical processes would have to be concluded before any positive statements could be made, but the following situation might occur.

It is well known that the replacibility of cations is $Na^+ < K^+$, that is, the equilibrium situation is that K^+ will be preferentially absorbed. However, the K/Na ratio <u>during</u> attainment of equilibrium may be considerably different than the equilibrium ratio as determined from the concentrations of Na and K in the sea water. That this is so may be seen from the following possible mechanism:

$$C + Na^+ \rightarrow C_{Na} \quad (1) \quad (\text{"C" representing "clay"})$$

$$C + K^+ \rightarrow C_K \quad (2)$$

$$C_{Na} + K^+ \rightleftarrows C_K + Na^+ \quad (3)$$

The Na/K ratio in sea water is about 25. It is then clear that initially, the reaction (1) would be about 25 times faster than (2) assuming essential similarity of rate constant. Initially then there would be a preponderance of Na^+clay, which excess would decrease continually, until finally the equilibrium situation is attained, at a ratio conditioned by reaction (3). Simultaneous solution of the three equations would yield that the form of the variations of Na^+/K^+ in time. However, the general form is qualitatively clear. Critical to this hypothesis is the relative rate of the exchange reactions and of sedimentation. The rates of many exchange reactions are extremely rapid, and hence the above is only a suggestion to be investigated.

Pursuant to the above theory of the relation of sodium content to rate of deposition, there is the well known geological relation of soda-rich hypabyssal rocks and extrusives to geosynclinal sediments. To quote Turner and Vechoogen (116 page 201):

> "Most eroded geosynclines show evidence of igneous activity approximately synchronous with at least the later part of the filling and sinking of the trough. Prominent among the products of such activity, and almost confinde to the geosynclinal environment, are submarine lavas, tuffs, and equivalent intrusives of sodic composition. These constitute the spilite keratophyre associations."

All geosynclines do not show spilitic rocks, and when spilitic rocks are present, normal basalts may be present also. Spilites are basic lavas consisting of sodic feldspar plus augite or its altered equivalent. Also characteristic of spilites is a low potassium content, which is again compatible with the above hypothesis. Indeed, a normal amount of K would invalidate the hypothesis.

A possible explanation of the spilite type, and one that has long been suggested is that they are formed by the action of sea water on normal basaltic magma, at the time of intrusion. This hypothesis is similar to the above, but is more limited, and does not explain why not all marine basalts are spilitic. For discussion of this theory see Turner and Verhoogen (116 page 203).

It is clear from the qualitative discussion of the mathematics that rapid deposition and burial of sediments, bringing exothermic reactions into "insulated zones, will favour metamorphism. This may be one reason for the high soda content of metamorphic rocks. This rate of deposition cannot be the only explation for metamophism. since in the Caledonian geosyncline, the metamorphic axis does not appear parallel to the equal-depositional-rate lines. (Kennedy 57).

One final point relating to the sodium economy of sediments is the relation of the above hypothesis to the characteristically low ages for the ocean based obtained by the sodium method. A hitherto-unappreciated loss of sodium in certain types of deposition could explain the anomaly.

3. Granitization.

A. General

The granitization controversy has become increasingly prominent in recent years. Interest in it is not limited to the particular petrologic features of granitization, fascinating though they are. Rather, because of the major role which granitic rocks play in geology as a whole, the problem is perhaps the most pressing of the day, geologically.

There have been so many recent treatments of the history and general features of the argument that it would be quite superfluous to give any background here. Illustrious names in geology are ranged on both sides, and it is obvious that there has yet been no overpoweringly convincing evidence either way. The most reasonable view at present seems to be expressed by the now famous remark of Reade "there are granites and granites". The purpose here is, initially, to stress the consequences which chemical energy may have for the problem, and then to discuss particular features of the problem in more detail.

In the writer's opinion, the main obstacle before a more general adherence to granitization as an origin for granites is the lack of a physically visualizable mechanism. As far as evidence for granitization having occurred is concerned, there is if anything a superfluity of examples, and the list is increasing yearly. However, explanations of how and why granitization has taken place have been satisfactory to but a very minor number of geologists.

In particular, the energy problem for granitization, as now pictured, is equally as formidable as it is for the magmatic theory. Added to this is the appeal to diffusion of chemical elements over long distances to account for various compositional data, which theories, as usually stated, have very small attraction for field geologists. Diffusion over short distances, of the order of millimeters or centimeters, has clear and unequivocal support in metamorphic phenomena. Diffusion over long distances is in quite another category, being certainly outside the realm of our present geological field or laboratory experience.

Broadly, the hypothesis of chemical energy offers a solution to the problem of the mechanism. There is with this hypothesis no necessity of bringing energy into the region of interest. Also, from the previous section, it is seen that there may be no chemical addition required. According to this hypothesis, granitization is a sort of spontaneous combustion, the initiation and character of which depend on local chemical, mechanical, and thermal factors.

Such factors may be, of themselves, ineffective as geologic agents, yet, by stimulating reaction, trigger off large amounts of energy. The role of radio-activity - in the crustal region - may be of this character. It is certainly so that many granites are highly radioactive. Whether this is of genetic significance, or merely incidental, might be decided by more detailed investigation.

Many of the small-scale features of granitization can be explained on this basis, for instance, streaked gneisses and schists. This metamorphic differentiation has frequently been discussed in the literature (70).

Such streaks would be initiated by perhaps quite minute local differences in composition and grain character, which would either favor reaction slightly, or would result in increased heat of reaction. It is then clear that there would be a strong tendency for the feature to perpetuate and accentuate itself, by causing diffusion of reactive material and hence achieving metamorphic differentiation.

Striking evidence of the influence of local composition and nature of the reactive material is provided by "metamorphic reversal" of graded bedding. Professor Shrock, to whom the writer is indebted for pointing out this relation, cites numerous examples (96B). The same reference provides a good example of the small amount of deformation which accompanies many metamorphic processes.

Evidence of the effect of original composition and structure on a broader scale is cited in almost every paper on granitized areas. A particularly clear case has been described by Misch (73), in the Nanga Parbat area of the NW Himalayas, where the original beds can be traced into the metamorphic zone. In particular, the calcareous beds are stated to have experienced practically no alteration (p224).

It is not necessary to cite further instances of general granitization, as there is no lack of descriptions in the literature. With regard to granitization, or rather transformation, involving volcanic materials, less has been done. It is therefore appropriate to cite the following interesting cases.

Holmes discusses the formation of lava in situ from tuff as occurring in Uganda (45). He considers the embryonic cones described to occupy the sites of unusually hot fumaroles. It is unlikely that all the effect could be due to surface energy of the tuff, but it would be interesting to have a closer evaluation of the problem with this effect in mind.

Judd (53), in 1889 published upon the growth of crystals of feldspar at the expense of glass in hypabyssal rocks. He considers that there is clear petrographic evidence for this growth, and among other conclusions, considers that miarolitic cavities in such rocks are due to the contraction attendant upon the phase change.

A more well known case, and one of which the writer has some personal knowledge, is that of the Sudbury granophy-re. In recent years, a granitization origin has been postulated for the granophy-re. - e.g. Yates (126). The general features of the area are well known, and Yates discusses evidence for granitization. Here, on a general scale, it is only noted that devitrification of the rhyolitic lavas of the Whitewater (given their presence) would be an exothermic reaction.

In more detail, the Whitewater-granophy-re contact is of interest to the present paper. This contact has associated with it a mixed rock which is sometimes locally called an agglomerate. This agglomerate consists of discrete ovoids of coarse granophyre, of remarkable constancy in appearance, set in a groundmass of fine, locally granophyric lava of acidic composition. This matrix grades into lava lacking the granophyric pods, and itself shows a flow breccia or agglomeratic structure.

A coherent detailed description would be excessively lengthy, and will not be attempted. From several weeks detailed study of such contacts, the writer submits that they represent a normal stage of granitization of the original agglomerate-flow breccia. The interpretation is that granitization occurred selectively, as a result of local excessive glassiness, or local compositional differences. This is definitely compatible with the field facts. The assumption that the granophyric fragments are actual agglomeratic pods is rendered impossible by the occurrence, in many areas, of "fragments" up to two hundred feet in diameter.

It may be suggested in regard to this hypothesis that the minute differences in composition and texture of the original material would not cause such bold differences. The best reply would be that the field facts indicate that the initial variations actually are able to do so. In another vein, the writer feels that the situation is analogous to that shown by the above-mentioned streaked gneisses, and that it would be surprising if such "agglomerates" were not found in granitization of the material in question. (That is, if the "chemical" mechanism for the gneisses is correct).

Another objection might be that granitized contacts would not be sharp. Again, one answer is that a number of them definitely are sharp. Less polemically, regions in which there are sources are much more likely to have sharp "wave fronts" - see page 105 - than are inert media. In the latter the controlling factor would be diffusivity alone. The actual sharpness of the reaction contact could be calulated as indicated in section VIc, but it is perhaps sufficient to give examples of analogous simpler situations. Thus the temperature gradient across the char front of a burning block of wood is much sharper than would be a conductivity gradient in the same material below the ignition point. There is also the influence of the type of initiating disturbance - thus the "rot front" of wood is usually hazy, despite the similarity of the net reaction to the burning reaction.

Another instance of metamorphic granophyre has been cited by Ellis (24) in South Africa. Many other minor instances have been noted in the Nothern Ontario pre-Cambrian by the writer, particularly as replacement of originally sheared rocks. Minor features of granophyric material are completely described by Drescher-Kaden (22A).

Discussion of granitization and the hypothesis of chemical energy would not be complete without a note that "classical" magmas could be accomodated as well. It is not possible to state definitely either the temperature rises obtainable by reaction, or those required to produce rheomorphism, because of lack of data, but the values given earlier (V) show that the possibility of magma formation by exothermic reaction must be at least considered. It is of course not necessary that every crystal should fuse - it is usual to consider a magma as a sort of crystal mush, in which a large part of the mobility is due to its acting as a chemical solution, and not merely a melt.

If fusion did actually occur, the highly endothermic latent heat effect would act as a temperature-stabilizing device, and such fusion might therefore be considered as a sort of natural thermal governor.

Quite aside from physico-chemical support, geologic evidence would suggest that any proposed mechanism should explain also "classical" magmas. Very few "transformists" deny the existence of <u>some</u> magmatic granite, at least small bodies of such. What must be decided is whether such ultrametamorphism can arise in rather normal metamorphic situations, or must be ascribed to the extra stimulation of external sources - as local stresses, heat flow,....which are not part of the common cycle.

b. Geosynclines.

The chemical energy hypothesis is particularly well adapted to explanation of metamorphism and granitization related to geosynclinal activity, as well as the indicated periodicity of such geosynclinal phenomena.

From what has already been said, it is clear that metamorphism should occur most readily in thick series of sediments in which rapid deposition has occurred. The hypothesis of spontaneous reaction predicts, rather than merely accomodates, many of the commonly accepted features of the geosynclinal cycle.

The periodicity of geosynclines would of course be related to the time of build-up of something of the nature of a critical mass. The effect of heat production in the geosynclinal prism might, moreover, have effects on convection in the mantle, as has already been mentioned.

On the basis of intrinsic chemical energy it is easy to explain the features of the "growth of continents" hypothesis which has recently received much attention. In particular, there is no difficulty in explaining why granitizing fluids, heat, or other energy is concentrated on the sedimentary bodies in question. In a contrary vein, metamorphism in a chemically -(chemical in the sense of page 20)- cannot be explained by intrinsic energy, and there should be no innate power of a second metamorphism of an area once metamorphosed.

Finally, it must be noted that the problem as a whole is by no means simple, and other crustal factors are surely involved. However, it is necessary to appreciate the intrinsic heat and volume effects which chemical energy can provide before the nature of the extraneous effects can be clearly evaluated.

The effect of volume change in metamorphism has been discussed by Perrin (81). On the basis of the formation of granite from quartzite by metasomatism, Perrin calculates a formidable volume increase, and uses this volume increase to explain folding. Perrin's example is an extreme case, as already mentioned. However, there is certain to be some volume effect. The present writer feels that this will in general take the form of an ultimate decrease in volume, because of the compact nature of most metamorphic silicates. Counteracting this effect will be the opposite one of thermal expansion, and it is difficult to make predictions regarding the situation during reaction. The problem is worthy of study, however, and might explain some of the dynamic effects commonly observed in geosynclines, as block faulting or, in the opposite sense, folding.

The effect of a minor volume change - in devitrification - has already been cited (page 143).

c. Mineral deposits and metamorphism.

In recent years, increasing attention has been directed to the relation between ore and granitization. Earlier, there has of course been a recognition of the frequent association of ore and metamorphism generally. Recent thought on the subject has been expressed by Sullivan (105), Goodspeed (37A) and others.

Essentially, it is recognized that crystallization of any mineral involves concentration of the constituent elements within the mineral grain, and simultaneous enrichment of the extragranular region in the remaining elements. In many cases, metallic elements such as the base metals cannot be accomodated into the structures of normal rock minerals in any appreciable amounts and are hence intergranularly concentrated, along with water of dehydrated structures, and other elements. The metallic elements have then been concentrated by a metamorphic differentiation process. Such a metamorphic differentiation occurs of course in all metamorphism, but because of the high mobility of such a metallic phase as postulated above, there is the possibility of further concentration by something akin to normal flow. In non-metallic phases this is less likely, but some pegmatites and similar small intrusives may be formed in this way.

So far little has been mentioned of the relation of chemical energy to the process. Indirectly, the chemical energy is related to the granitization, and provides the driving force for a truly spontaneous segragation. More directly, depending upon the manner in which the mass is granitized, there would seem to be vast differences in the fate of the metallic phase. If the crystallization were perfectly homogeneous - in time as well as space - throughout the mass, there would be but slight tendency for the metal phase to accumulate. In other words, there would essentially be no variation in temperature, or chemical potential to induce unidirectional diffusion. Over short distanes, the tendency to decrease surface energy would lead to coagulation, and superposed on all would be the rather constant pressure gradient.

Under other conditions, crystallization from a center would lead to metal concentration around the periphery, crystallization occurring in two shale beds separated by a limestone would lead to concentration in the limestone, and so forth. The presence of fractures would of course affect all the above. Given information regarding the initial composition of a body, and its environment, the nature of the associated mineralization might be predictable, if the parameters could be approximated.

On a less theoretical basis, recognition of the possibility of achieving energy release in situ might throw light on the true origin of such sedimentary-appearing deposits as the Rhodesian copper deposits, which are difficult to account for by the usual theories of metamorphism.

The role of exothermic reactions must also be considered in relation to the problem of the origin and concentration of petroleum. This problem is of course one of the major unsolved problems of the petroleum industry. That the ultimate source of the hydrocarbons is to be sought in shales or other rocks rich in organic material has long been suggested. It has also been recognized that, if an adequate source of heat were available, a distillation process could give rise to petroleum. However, so far as the writer is aware, there has been no entirely satisfactory mechanism conceived using "classical" sources of energy.

Chemical heat sources within the source bed, or in contiguous beds, would provide an adequate mechanism. This mechanism is entirely analogous to that discussed above relative to metal concentration, but the temperature required would be lower.

Distillation of this type - that is, distillation taking place in sedimentary beds in situ, is used by certain Swedish companies in recovery of oil from shale. The distillation itself is then not entirely hypothetical, and only the migration and concentration need be explained. Present theories on these latter points appear adequate.

The nature of the reactions causing the temperature rise may be of the types already discussed - that is, re-crystallization and reactions in the ordinary sense. It has already been mentioned, in discussion of authigenic albite in the Green River formation, that such albite was more frequently found in the beds richest in organic matter. The facts therefore do not militate against the possibility of reactions in such beds. On the contrary, the organic material is liable to provide a more mobile phase, which would abet the reaction process. This is suggested by the above occurrence.

CONCLUSION

Throughout this paper, the writer's plan has been to further consideration of the role of chemical energy in geology by elucidating the geologic origin and setting of the problem.

In essence, the hope is that the general theme has been made either sufficiently reasonable to lead the geologist to admit it as one of his working hypotheses, or sufficiently irritating to cause him to make some positive effort towards its invalidation.

It has been shown that it is certain that the chemical factor exists, and has <u>some</u> effect. The problem should now be to supplement the sparse data available and delineate the features of the effect more closely.

One feature of the hypothesis which is felt to be particularly compatible with geologic observation is that it is not simple. That is, depending on conditions, a multitude of different effects is possible within the general framework. A similar complexity is suggested by field occurrences, and in the writer's opinion, any hypothesis which cannot account for this complexity can be arbitrarily stated to be incomplete.

FURTHER WORK

It is obvious from the treatment given that much work remains to be done in each of the constituent parts of the problem:

1. Heat of transformation values
2. Rates of reaction
3. Mathematical traatment
4. Geological evidence.

Of these divisions, the most important, in the present state of affairs, are 1. and 4. . For unless there is an adequate heat source, or sink, there is no purpose in securing exact values of reaction rate and performing exact mathematical calculations, at least from the practical viewpoint. What is needed initially is addition to our knowledge of the heats of reaction, if only as regards order of magnitude, and, concurrently with such investigation, detailed geologic work conducted with the idea of chemical sources as one working hypothesis.

Such an approach is able to give a rapid evaluation of points discussed in the paper, and would lead to ideas concerning the important points to be treated in 2. and 3. .

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BIOGRAPHICAL NOTE

Vincent Alexander Saull was born in Montreal, Canada, on June twenty-fifth, 1927, the fourth son of John and Kathleen Saull.

Primary education was received at Luke Callaghan Memorial School, and at l'Academie Querbes in Montreal.

Junior matriculation was made from the Catholic High School of Montreal. During this period, a four-year tuition scholarship was held, and a number of scholastic honors won.

In May, 1948, the degree of B.Sc., honours Geological Sciences, was awarded by McGill University. Several one-year scholarships and bursaries were held during the undergraduate period.

During the period 1948-1952, the academic year was spent in graduate work at the Massachusetts Institute of Technology, towards the Ph.D. degree in Theoretical Geophysics. A Research Assistantship under Dr. P.M. Hurley was held during the term 1948-49. Teaching Fellowships were held during the term 1949-50, and during the fall term, 1951, under Dr. P.M. Hurley, and Dr. M.J. Buerger, respectively. A special scholarship from the National Research Council of Canada was held during the academic year 1951-52.

Six summers have been spent in field work in Canada - five in various types of geologic mapping, and one on a reflection seismograph crew.

Junior membership is held in the Canadian Institute of Mining and Metallurgy, Associate membership in the American Geophysical Union, and Membership in Sigma Xi.

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