ON THE RELATION BETWEEN EXTERNAL PRESSURE AND RE-CRYSTALLISATION OF MINERALS

BY

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The thermodynamics of the Earth's crust have recently been treated in several Norwegian papers, notably by H. Ramberg (1— 2—3) and by Jens Bugge (4). One of the principal conclusions of these papers is, that the chemical activity (the chemical potential, vapour-pressure) of a substance will increase with increasing pressure. Consequently, all minerals which are subject to stress will show a tendency to re-crystallize. This re-crystallisation must take place in the way that the ions of the mineral are transferred to a disperse phase in places of high pressure and condense to a consolidated orderly phase when the pressure is lower. The result will be a diffusion from high to low pressure; whether this diffusion takes place through the consolidated phase or through the disperse phase is left undecided. Ramberg points out that the relation between chemical activity and pressure is given by the equation:

$$D = Ke^{\frac{M(P - D_T) - \Delta FS}{RTS}}$$

or equivalent equations.

That the activity will increase with increasing pressure is in itself not new, but a commonly known fact to the chemist. There is probably no special objection to the equations used by Ramberg and Jens Bugge, nor are the equations new ones. Certain objections must, however, be raised against their application to geological phenomena, as these applications do not always seem to be consistent with natural conditions. It is quite correct that the chemical potential of a pure substance will increase at increased pressure. One should, however, realize that this generally applies only to pure substances and is not necessarily valid if the ions or molecules of the substance are affected

by another substance which is present.   This may be illustrated in the following manner. If pressure is exerted on a crystal by a gas or liquid which has no influence on either the crystal or its vapour (dissolved particles), then increased pressure by this inactive gas (liquid) will increase the vapour pressure (solubility) of the crystal exponentially, according to the equations used by Ramberg and Bugge. This increased vapour pressure (solubility) may be explained through a lowering of the difference in the energy states of an atom in the consolidated and in the disperse phase by increased pressure.   Quite different conditions will, however, arise if pressure is applied through the medium of a gas or a liquid which attracts or repels the particles of the crystal.   If attractive forces exist between the particles of the gas or liquid and those of the crystal, then an increased pressure of the said gas or liquid will increase the tendency of the particles of the crystal to pass into the disperse phase, and the equilibrium concentration of the vapour phase (solution) will increase more rapidly with pressure than indicated by the equation. If, on the other hand, a gas or liquid which has a repulsive influence on the particles of the crystal is used, an increased pressure will reduce the tendency of the particles to pass into the disperse phase, and the equilibrium concentration in the vapour phase (solution) may decrease with increasing pressure. The relation between the chemical potential and the concentration at constant temperature and pressure is given in the equation

$$\left(\frac{d\,\mu}{d\,c}\right)_{TP} = \Delta Q \left(\frac{\partial T}{\partial c}\right)_P K.$$

Δ Q here represents the heat of solution.   It will be seen that $\left(\frac{d\,\mu}{d\,c}\right)_{TP}$ will always be positive, because if Δ Q is positive, then $\left(\frac{\partial T}{\partial c}\right)_P$ will be positive, and if ΔQ is negative, then $\left(\frac{\partial T}{\partial c}\right)_P$ will be negative.

An increased concentration will consequently result in an increase of the chemical potential at constant temperature and pressure. Now the connection between chemical potential and chemical activity is given by the equation: $\mu = RT \ln a + K$. An increase of the chemical potential will result in an increase of the activity. Since activity, concentration and chemical potentila are symbate quantities, it is unimportant which of them we use for a purely qualitative discussion. The

chemical potential and the concentration will be simply proportional within a short interval (of variation). The chemical potential of a saturated solution relative to the pure solute will be equal to the chemical potential of the pure solute relative to the solution. The variation of concentration with pressure, at constant temperature, is given by the equation:

$$\left(\frac{d\,c}{d\,p}\right)_T = \frac{V_1 \div V}{\left(\frac{d\,\mu}{d\,c}\right)_{PT}} \cdot K.$$ Here $V_1 =$ the partial volume of the solute in

the solution and $V =$ its specific volume in the solid state. I have given this equation in a slightly different form in a previous paper (5), and it is the only equation required for a discussion of the effect of pressure on the recrystallisation processes, when there besides the solid also is present a fluid which acts as a solvent for the disperse phase, regardless of whether this fluid is a gas or a liquid. On the other hand, the reasoning of Ramberg and Bugge is valid only in case there is one chemical compound, or the other compounds present exercise no influence on the chemical potential of the substance in question. This is scarcely ever the case in nature, but only at e. g. recrystallisation of a pure metal in a vacuum.

Both Ramberg and Bugge suppose that in the Earth's crust the disperse phase (solution or vapour) and the solid mineral in contact with the disperse phase will be subject to very different pressures. They thus maintain that the disperse phase is subject to a pressure which is equal to the superimposed disperse phase + the pressure on the surface of the earth, whereas the solid mineral is subject to a pressure equal to the weight of the superimposed rock + the pressure on the surface of the earth. Whether this ever will be the case seems very doubtful, except for comparatively large open fissures filled with the disperse phase right up to the surface of the earth, and even then there will be no pressure-difference on the surface of contact between the disperse phase and the solid mineral, but instead a stress in the mineral. This type of open fissures is very rare in rocks. The disperse phase is probably as a rule found as a very thin intergranular film of a thickness varying from a few Ångströms to a couple of hundred Ångströms. Here adsorbtion phenomena will take place, and the disperse phase may have a high degree of rigidity. This makes possible large pressure gradients of a very local nature, e. g. between two areas of the surface of one crystal.

In ideal solutions a substance will dissolve in another substance without any change in the total volume or the temperature. In real solutions there will, however, appear a heat of solution, positive or negative, at constant pressure. At constant temperature there will further be a change in volume, either positive or negative. If a crystal with surrounding disperse phase is subjected to a pressure pradient at constant temperature, there may therefore arise two opposite cases, with an intermediate case where the effects cancel.

C a s e I: Assume a crystal with surrounding disperse phase. This disperse phase is a saturated solution of the crystal's ions in a disperse medium (liquid or gas). It is further assumed that this crystal is of such chemical composition as to dissolve in the medium under volume contraction. Should this crystal with surrounding disperse phase become subject to a certain pressure gradient, the crystal will respond to this stress by sending ions into solution at the point subject to the highest pressure. .The result is a reduction in the combined volumes of crystal and liquid. The increased concentration of the solute will increase the chemical potential of the solution, and a diffusion will take place to the parts of the disperse phase where the pressure is smaller, because the concentration, and consequently the chemical potential, will be smaller there. In this manner the solution will, however, become super-saturated relative to the lower pressure, and a precipitation of the dissolved ions will take place. It may be differently said that the place of least pressure will act as a cold wall and condense the diffusing ions. This diffusion will continue until the difference in pressure has been cancelled by the re-crystallisation, or until the solvent has been completely expelled from the space which it occupied. This form of diffusion is easy to conceive, as it operates from high pressure towards low pressure. It is consistent with the conditions as stated by Ramberg and Bugge, although on a slightly different basis.

C a s e I I: Assume a crystal with surrounding disperse phase. As in case I this disperse phase is a saturated solution of the crystal in some other disperse medium (liquid or gas). It is further assumed that this crystal is of such chemical composition as to dissolve under expansion. Should this crystal with surrounding disperse phase become subject to a certain pressure gradient, the crystal will respond to this stress by the precipitation of ions from the solution at the point of highest pressure. The result is a reduction in the combined volumes

of crystal and liquid. The decreasing concentration of the dissolved matter will, however, reduce the chemical potential of the solution, and at the same time the increased pressure will increase the chemical potential. Provided the first of these effects is the stronger, a diffusion will take place from the parts of the disperse phase where the pressure is lowest since the concentration and consequently the chemical potential is at the highest there. The result is that the solution will become supersaturated at the places of higher pressure causing a precipitation of the dissolved ions. At the places of lower pressure the solution will become unsaturated, and the solid matter will be continually dissolved. It may be said that the place of highest pressure will act as a cold wall and condense the diffusing particles. This form of diffusion may at first seem a little more difficult to understand, as the diffusion takes place from low to high pressure. It is, however, strictly in accordance with the principle of le Chatelier, since the response to an increased pressure will be a reduction of the total volume at the point subject to the greatest pressure.

It may perhaps be easier to illustrate the recrystallisation processes energetically: As model one may imagine a tube made from some substance soluble in water with a change in volume. The tube is filled with a saturated solution of the substance in water and parted in the middle by a wall which does not permit the free transmission of pressure, but allows the ions of the solute and the ions of the solvent to pass. By means of a pressure-reservoir one keeps constant pressure $= P + \Delta P$ atm. on one side of the wall, whereas the pressure is kept at P atm. on the other side. Assuming the solute in its pure state to have a molvolume $= V$ and in its dissolved state a molar partial volume $= V + \Delta V$, it will require an energy $= P. \Delta V$ 1 atm. to dissolve one gramme-molecule of the matter at the pressure P. When one grammol of the substance is crystallized at the pressure $P + \Delta P$ an energy $= (P + \Delta P). V$ 1 atm. is liberated. A solution of one grammol of the substance at the pressure P and precipitation at the pressure $P + \Delta P$ gains an energy $= \Delta P. \Delta V$ 1. atm. This process will consequently progress spontaneously provided ΔP and ΔV both are positive or negative. This means that, provided the partial volume in the dissolved state is greater than the molvolume in the pure state, energy will be liberated by recrystallisation from low to high pressure. This recrystallisation will continue until all solvent

has been expelled from the places where pressure is high or the pressure has been equalized through the recrystallization process.

If we next imagine a tube with walls consisting of two different substances, one of which is just as much more easily soluble at high pressure than at low pressure as the other is less soluble at high pressure than at low pressure, the diffusion process will, provided the pressure difference is kept constant between the two sides of the partition, continue until the substance which is most soluble at high pressure has been quantitatively transferred to the place where the pressure is lowest and vice versa. If we have two substances the solubilities of which are affected differently by pressure, a mixture of these two with a solvent may thus result in replacement phenomena when stress is applied to the whole system. When the pressure is highest, the substance the solubility of which increases more slowly, or decreases with increasing pressure, will replace the substance with the more rapidly increasing solubility and vice versa.

All the above observations are based on the assumption that the temperature is constant and the minerals are exposed to stress. A quite analogous discussion is possible in case the pressure is kept constant while the minerals are exposed to a difference in temperature. Exactly in the same manner as the variation of the concentration with the pressure is a function of the change in volume at solution it will be found that the variation of the concentration with temperature is a function of the heat of solution.

It is not possible to tell without laboratory tests how the solubility of a mineral varies with pressure, because, the presence of other dissolved substances in the solvent plays an important part. The majority of substances are less soluble in water at increasing pressure, but e. g. the salts of some acids with alkalis become more soluble in water at increasing pressure. Since the presence of alkali-ions in the solvent exercise a strong influence on the solubility of e. g. silica and alumina, one may increase the solubility of these substances with increasing pressure by using e. g. a mixture of alkali carbonate and aluminium-hydroxide, as the solubility of the alkali carbonate will increase rapidly with increasing pressure. A number of natural minerals are known which show a tendency to grow against increasing pressure, as e. g. staurolite and chloritoid. I have previously described (5) how these minerals may be found as porphyroblasts in schistous rocks with their longest extension vertically on the schistosity,

in other words parallell with the pressure gradient. Considering that
the substances which build up these materials are less soluble at high
than at low pressure this is to be expected. In the same rocks will
be found felspar porphyroblasts with their longest extension parallell
with the schistosity, in other words apparently orientated vertical to
the pressure gradient. This is also reasonable because the alkali
compounds generally have their maximum solubility at high pressure.
We know the principles which govern these processes, but lack exact
data for the separate cases. Nature's own laboratory as represented
by the rocks which are accessible to observation gives us a fair indic-
ation as to the trend of the various processes, and a careful study of
the natural rocks may give valuable results, but it would naturally be
still better to have these processes properly examined in laboratories
under controlled conditions.

I repeat that I do not consider the equations used by Bugge and
Ramberg as faulty but their application of these equations as incorrect.

The equations have been derived for, and are valid for, conditions
which are never, or at the very best extremely rarely, realized in the
Earth's crust and least of all in the metamorphic rocks. One can thus
hardly conceive that there will in reality exist different pressures on
the surface of a crystal and on the fluid phase where the two are in
contact. Ramberg assumes that pressure is applied on a crystal with
a piston, which the ions of the crystal can penetrate when they are in
a liquid or gaseous state. That a piston of this nature exists would
not mean that there will be a difference of pressure between the con-
solidated and disperse phase where these are in contact with each
other. The case may be illustrated by imagining a vessel filled with
metal balls (spheres) and a liquid. The liquid represents the dissolved
disperse phase, whereas the balls (spheres) represent the crystal(s).
Where there is contact between liquid and ball (sphere) in one of
the interstices in the random packing of the spheres, the pressure will
obviously be equal to the weight of the super-natant liquid on both
the liquid and the metal spheres. On the point of contact between
two spheres the pressure will, however, be equal to the weight
of the superimposed spheres plus liquid. If liquid is absorbed to
the spheres at their contact points, this thin film will naturally also
be exposed to the same pressure. If the forces of absorption are
smaller than the pressure gradient which will exist in the film be-
tween the points of contact and the liquid-filled inerstices, the entire

liquid phase will be expelled from the contact points, and the spheres will now rest with metal against metal without any gap, as if they were one piece. Nor will we in this case have any disperse phase in contact with a consolidated phase of a different pressure. One should be aware of the essential part played by adsorption forces for the thin liquid layers which we find as intergranular films in the common rocks. Thus water which is bound by absorption to the surface of a clay particle to a layer which is about 500 Å thick will have a cutting resistance of a couple of grammes per sq. cm. When the absorbed water layer is 100 Å thick its cutting resistance is nearly 1 kilo per sq. cm. This means that the intergranular film in the rock has mechanical properties between those of glue and glass. It is therefore easily understood that a stress in the rock will be followed by stress also in the disperse phase. I have also before emphasized this (5). It is obvious that the nature of the solvent which forms the disperse phase plays an important part for the recrystallisation process and the transportation of matter. One may also effect recrystallisation processes in the opposite direction by a suitable choice of solvent for the disperse phase. One may easily obtain recrystallisation from a crystal with low vapour pressure to a crystal with high vapour pressure.

Just as the solubility of a substance in another at constant temperature but at varying pressure is a function of the change in volume by solution, the effect of the temperature at constant pressure on the solubility is dependent on the heat of solution. Consequently a substance with positive heat of solution will be less soluble at high temperature than at low temperature. As an example one may take $Ca(OH)_2$. At 15° C 1.22 grammes will dissolve per liter of water, at 95° C 0.58 gramme per liter of water. If water and excess $Ca(OH)_2$ are sealed in a tube, one end of which is held at about 100° C and the other at room-temperature one will get a recrystallisation of $Ca(OH)_2$ from the cold end of the tube to the hot end, even if the latter is at a higher level and the middle of the tube is filled with cellulose slime. Since $Ca(OH)_2$ is dissolved under liberation of heat and crystallized with absorption of heat, the recrystallisation will entail an increase of entropy. The experiment is easily made and requires hardly any equipment. In the course of a few days one will notice well-developed $Ca(OH)_2$ crystals in the hot end of the tube. Provided no water has been present, there would be a, admittedly very slow, sublimation from high to low temperature. Since the disperse phase in rocks al-

ways has a composition which is different from that of the crystalline
phase(s), the discussions of Ramberg and of Bugge will have purely
theoretical interest, except for reactions which take place in the solid
state, in which case the disperse phase is not present. Repeated in-
vestigations have shown that a migration of ions takes place many
times more quickly in a disordered phase (solution of gas) than
through an ordered crystal-lattice, and all the known rocks have inter-
granular fissures offering the possibility of the presence of a disperse
phase.

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1. H. Ramberg: Vid.-Akad. Oslo. Avh. I, 1944, No. 3.
2.   »   N. G. T. *24*, 98, 1945,
3.   »   G. F. F. Stockh. Jan.—Feb. 1946.
4. J. Bugge: Vid.-Akad. Oslo. Avh. I, 1945, No. 13.
5. I. Th. Rosenqvist: Om øyegneisdannelse i fjellkjeden N. G. T. *21*, 165, 1941.