A THEORETICAL CONSIDERATION OF IDEAL LIQUID INCLUSIONS.[1]

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ABSTRACT.

Geologic thermometry, as indicated by liquid inclusions, is analyzed mathematically by the consideration of ideal cases. The inclusions are divided into two groups; namely, those in which the included material was liquid at the time of being formed and those in which a gas was enclosed during formation. Utilizing the laws of expansion and contraction and the ideal gas laws, expressions are derived for the temperature of formation. The extent of erosion and the degree of tilting are also calculated for formations containing inclusions of the second kind.

Liquid inclusions in crystals have been used as a means of estimating the temperature of formation of mineral deposits. The classical work of Sorby (1) was the first in this interesting field of geologic thermometry and subsequent important contributions by such investigators as Holden (2), Newhouse (3), and others have materially added to our knowledge of the subject. An excellent literature review of this field is given in "The Composition of Vein Solutions As Shown by Liquid Inclusions in Minerals," by Newhouse (3). All of these estimations and calculations are based upon a knowledge of the thermodynamic properties of the included material and the mineral proper. For an accurate mathematical analysis it would be necessary to know these properties from the temperature of formation to room temperature.

The simplest case is the one in which the included substance in the liquid state was shut in by the crystallizing mineral. This case depends on the fact that the coefficient of expansion of the liquid is greater than that of the mineral and on cooling the liquid shrinks away from the mineral. If we postulate that both the liquid and the mineral have a constant coefficient of cubical expansion, in the range from room temperature to the temperature of formation, we can determine the temperature of formation by a very simple calculation.

[1] This paper is a mathematical study of highly idealized cases and consequently involves many simplifications which are departures from the actual. No claim of finality is made for the work but it is hoped that it will lead to a better understanding of the problem.

Let V_0 and V_t = volume at room temperature and temperature t.
α = coefficient of cubical expansion
the subscripts "L" and "M" designate the liquid and mineral
25° C = room temperature

Then $$(1)\ V_{t_L} = V_{0_L}(1 + \alpha_L\,[t - 25])$$

and $$(2)\ V_{t_M} = V_{0_M}(1 + \alpha_M\,[t - 25])$$

At temperature t (the temperature of inclusion)

$$(3)\ V_{t_L} = V_{t_M}$$

Then $$(4)\ V_{0_L}(1 + \alpha_L\,[t - 25]) = V_{0_M}(1 + \alpha_M\,[t - 25])$$

Solving for temperature t, we have

$$(5)\ t = \frac{1 - \dfrac{V_{0_L}}{V_{0_M}}}{\dfrac{V_{0_L}}{V_{0_M}}\alpha_L - \alpha_M} + 25$$

Let $$(6)\ K = \frac{V_{0_L}}{V_{0_M}}$$ and B = room temperature

Then $$(7)\quad t = \frac{1 - K}{K\alpha_L - \alpha_M} + B$$

The above equation requires the ratio of the volume of liquid to the volume of the cavity in the crystal. An examination of the mineral under the microscope only gives a ratio of the areas. Since the volume of similar figures varies as the three halves power of the area, we may write:

$$(8)\ \frac{V_{0_L}}{V_{0_M}} = \left(\frac{A_{0_L}}{A_{0_M}}\right)^{3/2} = K$$

The procedure in making a calculation should then be the estimation of several values of the ratio of the area of the liquid to the area of the cavity. After a statistical analysis of this data, the most probable value is substituted in the equation.

We have only considered the ideal case in which the coefficient of cubical expansion is a constant. Actually α varies

with t and therefore it would be necessary to substitute some variable which is a function of t. This would complicate the equation and in some cases make it insoluble.

Using the integrated form of the Clausius-Clapeyron equation, which gives the relation between vapor pressure and temperature, it is possible to calculate the minimum pressure under which such an inclusion may form.

$$(9)\quad \log_e \frac{P_2}{P_1} = \frac{E}{R}\,\frac{(T_2 - T_1)}{T_2 T_1}$$

P_1 and P_2 are the vapor pressures of the liquid in question at absolute temperature T_1 and T_2. E is the molar heat of vaporization over the range T_1 or T_2, and R is the molar gas constant. The vapor pressure of the liquid P_1 may be determined at some given temperature T_1 and our equation becomes

$$(10)\quad \log_e P_2 = \frac{E}{R}\,\frac{(T_2 - T_1)}{T_2 T_1} + \log_e P_1$$

Since all quantities on the right hand side of the equation are known ($T_2 = t + 273$, from equation (7)), it is possible to find P_2.

For example, let the included liquor be water and we will suppose that the crystallizing material is so insoluble that the small amount in solution does not lower the vapor pressure appreciably. (If some solute is present which does lower the vapor pressure considerably, its concentration should be determined and its effect on the vapor pressure calculated.) The vapor pressure of water at 100° C. or 373° absolute is one atmosphere. The heat of vaporization of water is 540 calories per gram or eighteen times that for one mole. In order to keep the equation dimensionally correct, R is set equal to two calories.

Then $$(11)\quad \log_{10} P_2 = 5.65 \left(\frac{t - 100}{t + 273}\right)$$

The pressure P_2 is then given in atmospheres. Care must be exercised in changing units in equation (11). The exact equation is equation (10). Our special case of equation (11) contains in reality the logarithm of one which is zero. If some other units were used, equation (11) would not hold.

A more complicated case of liquid inclusions is one in which the temperature of inclusion was high enough to keep the

liquid in question in the gaseous state. Our equation in this problem will contain two variables; namely, temperature and pressure. If either of the two variables were known the other could be determined. Another equation would be necessary in order to solve for both quantities.

As the inclusions were forming, those at a lower level in the formation were under greater pressure than those at higher levels. Consequently the ratio of liquid volume to the volume of the cavity should be greater for those at lower levels. This should then enable us to obtain two equations relating the pressures and temperature. (We must postulate that the temperature is constant throughout the formation.) Solving the two simultaneously will give the value of the two unknowns.

The solution depends on knowing the difference in pressure of the two inclusions at the time of formation. If the density of the mineral and the vertical distance between the inclusions were known at the time of formation, it would be possible to calculate this pressure difference.[2] If the formation is tilted (and this must be known) the actual vertical distance will not be that measured. A method somewhat as follows must be used in order to determine this vertical distance. Choose some exposed portion of the formation which is in the form of a dihedral angle whose vertex is as nearly vertical as possible. With some point on the vertex as a center, draw a semicircle on each of the faces of the angle. Samples should then be taken at the center and at appropriate positions on the semicircles. The radius of these circles and the angle a given sample makes with the center sample and the vertex line of the dihedral angle should be recorded. Other pertinent data such as the size of the dihedral angle and the orientation of the vertex with respect to a true horizontal plane must be noted.

The ratio of the volume of the liquid to the volume of the cavity will be a constant for all inclusions that lie along a line which is contained in a plane parallel to the original horizon. Comparison of this ratio in the center sample and the samples taken on the two semicircles will establish two orienting lines which intersect at the common center of the two semicircles.[3] These two intersecting lines will determine

[2] Postulates hydrostatic equilibrium.

[3] Interpolation may be resorted to in order to obtain an orienting line as almost an infinite number of samples would otherwise be necessary.

an orienting plane which is parallel to the horizon of the formation. The original vertical distance between samples can now be found as this distance is measured along lines perpendicular to the horizon of the formation.

The size of the radius of these sample semicircles should be such that the ratio of the pressures, in the inclusions to be used in the calculations, shall be as far from one as possible. If the inclusions were formed under fairly low pressures; that is, near the surface of the molten mass, a small difference in depth would change the ratio markedly. On the other hand, if the depth is great, it would take a considerable difference in depth to show much change in the ratio. Some scientific guessing is therefore necessary to determine this radius, but it is safe to make it as large as possible.

If we use the same symbols in this derivation as in our previous one we have:

$$(12)\quad V_{t_M} = V_{0_M}\,(1 + \alpha_M\,[t - 25])$$

We shall suppose that the enclosed vapor obeys the ideal gas laws (not an actual case).

Then $(13)\quad PV = nRT$

P, V, and T are respectively the pressure, volume, and absolute temperature of the gas. R is the molar gas constant and n is the number of moles.

$$(14)\quad n = \frac{g}{M}$$

g is the number of grams of the substance, and M is the molecular weight.

If V_{0_L} = the volume of this vapor when condensed to a liquid at room temperature, and d_L = the density,

Then $(15)\qquad n = \dfrac{V_{0_L}\ d_L}{M}$

And $(16)\quad PV_{t_v} = \dfrac{V_{0_L}\ d_L}{M}\ .\ R(t + 273)$

V_{t_v} = volume of the vapor at the temperature of solidification.

Solving equation (16) for V_{t_v} we have

$$(17)\quad V_{t_v} = \frac{V_{0_L}\, d_L\, R(t+273)}{MP}$$

But $(18)\quad V_{t_M} = V_{t_v}$ at the time of solidification.

Therefore equation (12) may be set equal to equation (17)

$$(19)\quad V_{0_M}(1+\alpha_M[t-25]) = \frac{V_{0_L}\, d_L\, R(t+273)}{MP}$$

$$(20)\quad \frac{V_{0_L}}{V_{0_M}} = \frac{(1+\alpha_M[t-25])\, MP}{d_L\, R(t+273)}$$

For a liquid inclusion at a lower level in the rock we have a corresponding equation whose pressure is increased by the difference in head under which the two inclusions in question were formed.

Then $(21)\quad \frac{V'_{0_L}}{V'_{0_M}} = \frac{(1+\alpha_M[t-25])\, M(P+h_t d_{t_M})}{d_L\, R(t+273)}$

The new ratio of the volume of liquid to the volume of cavity is designated by $\frac{V'_{0_L}}{V'_{0_M}}$ and h_t and d_{t_M} represent respectively the vertical distance between the two inclusions and the density of the molten mass at the temperature of solidification.

Solving equations (20) and (21) for P, we have

$$(22)\quad P = \frac{V_{0_L}}{V_{0_M}} \cdot \frac{d_L\, R(t+273)}{(1+\alpha_M[t-25])\, M}$$

$$(23)\quad P = \frac{V'_{0_L}}{V'_{0_M}} \cdot \frac{d_L\, R(t+273)}{(1+\alpha_M[t-25])\, M} - h_{t_M} d_{t_M}$$

Equating (22) and (23)

$$(24)\quad \frac{d_L\, R(t+273)}{(1+\alpha_M[t-25])\, M}\left(\frac{V'_{0_L}}{V'_{0_M}} - \frac{V_{0_L}}{V_{0_M}}\right) = h_{t_M} d_{t_M}$$

The density of the mineral and the vertical distance "h" given in our equation is that at the temperature of solidification. Since density varies inversely as the temperature, we have

$$(25)\quad d_{t_M} = \frac{d_{0_M}}{1 + \alpha_M [t - 25]}$$

And $$(26)\quad h_{t_M} = h_{0_M}\left(1 + \frac{\alpha_M}{3}[t - 25]\right)$$

$\frac{\alpha_M}{3}$ = coefficient of linear expansion.

Substituting (25) and (26) in (24)

(27)

$$\frac{d_L R(t + 273)}{M}\left(\frac{V'_{0_L}}{V'_{0_M}} - \frac{V_{0_L}}{V_{0_M}}\right) = h_{0_M} d_{0_M}\left(1 + \frac{\alpha_M}{3}[t - 25]\right)$$

Solving for t

$$(28)\quad t = 25 + \frac{298\, d_L RK - h_{0_M} d_{0_M} M}{\frac{h_{0_M} d_{0_M} M \alpha_M}{3} - d_L RK}$$

Where (29)

$$K = \left(\frac{V'_{0_L}}{V'_{0_M}} - \frac{V_{0_L}}{V_{0_M}}\right) = \left(\frac{A'_{0_L}}{A'_{0_M}}\right)^{3/2} - \left(\frac{A_{0_L}}{A_{0_M}}\right)^{3/2}$$

(see equation 8)

The temperature may now be determined as all of the other variables are known. h_{0_M} should be given in centimeters and $R = 8.7 \times 10^4$.

In our derivation we have considered that the gas was ideal at the temperature and pressure of inclusion. This is not true and strictly speaking we should use some equation of state for the gas instead of the ideal gas equation. Such a substitution would make the problem insoluble. We have also disregarded that portion of the included substance which is still in the vapor state at room temperature. In some cases this error may be appreciable.

Having determined approximately the temperature of the formation, substitute this quantity in equation (22) and the pressure under which the inclusion solidified will be obtained.

If it is postulated that the temperature of inclusion is the same as the melting point of the rock, as determined experimentally under atmospheric conditions, this value of t when substituted in equation (22) will give a value of P which corresponds to a pressure when the molten system is not under any external stresses. If the value of P based upon the experimental determination of t is different from the value of P based upon the calculated t, then some external force must have been operating on the system and the magnitude of this force will be measured by the magnitude of the difference in the pressures.

A very interesting speculation (and it should only be considered as such) arises in connection with such a possible difference in pressure. If we suppose that the only stress under which the formation was formed was atmospheric pressure, then we have a means of calculating that pressure at the time of formation. Calculations have been made on the rate of escape of the earth's atmosphere and this coupled with the difference in value of atmospheric pressure at the time of formation and the present, makes it possible to estimate the age of the formation.

The hydrostatic pressure on a given inclusion when formed is given by the equation:

$$(30)\quad P = H_t\, d_{t_M}$$

H_t is the distance from the inclusion to the surface of the molten mass and d_{t_M} is the density of the magma.

$$(31)\quad H_0\left(1 + \frac{\alpha_M}{3}[t - 25]\right) = H_t$$

And (32)
$$\frac{d_{0_M}}{1 + \alpha_M [t - 25]} = d_{t_M}$$

Therefore

$$(33)\quad P = \frac{H_0\, d_{0_M}\left(1 + \frac{\alpha_M}{3}[t - 25]\right)}{1 + \alpha_M [t - 25]}$$

Combining equation (33) with equation (22) and solving for H_0 we have

$$(34)\quad H_0 = \frac{V_{0_L}}{V_{0_M}} \cdot \frac{d_L R(t+273)}{d_0 M\left(1+\frac{\alpha_M}{3}[t-25]\right)}$$

If the melting point of the mineral is substituted for t in equation (34) it is possible to calculate the distance a given inclusion was below the surface of the formation after it had solidified and cooled. This calculation is also based on the supposition that no external forces other than atmospheric were acting upon the system at the time of solidification. The value of H_0 obtained from the above equation when compared with the measured value of the formation will give the extent of erosion.

Just as in the earlier case considered, as many estimations as possible should be made of the ratio of the areas of the cavity to that of the liquid. It might even be advantageous to study enlarged photographs with the aid of a planimeter. A statistical analysis of such data will determine the most probable value.

The question then arises as to which equation to use in calculating the temperature of formation. There are certain inclusions possible which outwardly may seem to be border line cases, the data of which when substituted in one of the equations, will give the correct result, or shall we say, the nearest to correct estimate in an actual case. This same data when substituted in the wrong equation will obviously lead to a false result.

A knowledge of other geologic data of the formation and its surroundings will aid in making a decision. For instance, if the included material were water, equation (7) would not hold if there were evidence that the temperature of formation was above 374° C., the critical temperature of water. Liquid water does not exist above this temperature. If the evidence were in favor of a temperature in this range, it must have been possible by some means or other to have had a pressure of about 218 atmospheres, the critical pressure of water, on the formation.

If the included material is liquid at the time of inclusion, the ratio of the volume of the cavity to liquid should be a

constant. This is, of course, postulating a constant temperature of formation. On the other hand, the ratio of the volume of cavity to liquid in our second type of inclusions is not a constant but varies regularly in going from elevation to elevation in the formation. An examination of equation (23) will show that plotting the ratio of the volumes against the vertical distance of separation in a given formation, will give a straight line. It would be extremely fortuitous and highly improbable that such an agreement would be found in the first type of inclusion.

SUMMARY.

1. Ideal liquid inclusions have been considered from a theoretical standpoint.

2. Equations have been derived to calculate the temperatures and pressures of formation of inclusions which were liquid at the temperature of inclusion.

3. Equations have been derived to calculate the temperatures and pressures of formation of inclusions which were vapors at the temperature of inclusion.

4. The magnitude of external stresses, the depth of the inclusion below the original surface of the formation and the extent of erosion may also be calculated for the second type of inclusion.

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