The entropy paradox and overstepping in metamorphic reactions

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A B S T R A C T

It is commonly asserted that entropy tends towards a maximum at equilibrium in isolated systems. But entropy is only defined in equilibrium states, so in an isolated system the entropy is constant, if it is defined at all. The solution to this paradox is the existence of metastable equilibrium states, so common in mineralogy and petrology. Consideration of such states in a thermodynamic context also involves the concept of constraints and of the affinity, and because the affinity is a measure of the change in Gibbs energy in spontaneous reactions involving metastable phases, the entropy paradox and the overstepping of reactions in metamorphic rocks are closely related subjects.

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1. Introduction

The property of entropy most important to the treatment of spontaneous or irreversible processes is that in an isolated system (one having a constant internal energy U and volume V) entropy can only increase, and reaches a maximum at equilibrium. For example, DeVoe (2012, p. 128) says

> The entropy of an isolated system continuously increases during a spontaneous, irreversible process until it reaches a maximum value at equilibrium.

However, if at the same time we consider the fact that in classical or equilibrium thermodynamics entropy is only defined in equilibrium states (see e.g. Pippard, 1966, p. 104; Sklar, 1993, p. 24, many others) we have a paradox, stated for example by Tisza (1966, p. 41):

> Gibbs stated the extremum principle in two versions: *In an isolated system the entropy tends to a maximum at constant energy, or alternatively, the energy tends to a minimum at constant entropy.*

Although these statements undoubtedly express important truths, they lack precision to the point of being paradoxical. If an isolated system is not at equilibrium, we can associate no entropy to it, and if it is in equilibrium, its entropy can no longer increase.

and (p. 120–121):

> The nature of this problem is illustrated by the following paradox: How are we to give a precise meaning to the statement that entropy tends toward a maximum, whereas entropy is defined only for systems in equilibrium? Thus in an isolated system, the entropy is constant, if it is defined at all.

2. The differential expressions

This paradox can be illustrated in a mathematical way. No matter in which way the Second Law is presented, the following differential expressions for isolated systems are commonly derived:

$$dS_{U,V} = 0 \quad \text{at equilibrium,} \tag{1}$$

$$dS_{U,V} > 0 \quad \text{for irreversible processes,} \tag{2}$$

or in general

$$dS_{U,V} \geq 0. \tag{3}$$

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Each of these differential expressions implies the existence of a third independent variable governing the value of S. For example Eq. (1) says that in an isolated system entropy is a continuous function of at least two independent variables, U and V, and exhibits an extremum (a maximum as shown by Eq. (2)) at equilibrium. As U and V are constant, S does not exhibit this maximum with respect to either one, so there is at least one more independent variable with respect to which S exhibits a maximum. In other words there must be an inverted-U shaped curve showing S as a function of some variable not yet defined, and every point on this curve must have S and indeed all thermodynamic properties defined. They are equilibrium states of the system, but not the most stable equilibrium state, which occurs at the maximum. They can be called *metastable equilibrium states*. An example of such a curve is shown in Fig. 3; see also de Heer (1986, Fig. 17b) for a schematic example. The existence of these states provides the solution to the paradox.

3. Activation energy

The existence of these metastable equilibrium states raises a question as to what prevents the system from spontaneously changing to a more stable state, with its accompanying energy (or entropy) change. Energy changes in real systems and in thermodynamic systems (i.e. the equations of thermodynamics) provide somewhat different ways of answering this question. In real systems the reason is usually that there is a kinetic barrier, an activation energy which must be overcome for the change to take place. Commonly this can be achieved by increasing the system energy, i.e., by raising the temperature. In rocks undergoing metamorphism the kinetic barrier is overcome by an increase in the energy difference between reactant and product phases, which occurs when the T–P conditions of the rock system change progressively away from an equilibrium boundary into a field where some or all of the reactant phases are metastable, a process known as overstepping which is illustrated in Fig. 1 (Waters and Lovegrove, 2002; Pattison et al., 2011).

However, there is no term or variable in thermodynamics for activation energy.[1] In thermodynamics energy changes are represented by fundamental equations such as Eq. (4),

$$dG = -S \, dT + V \, dP \qquad (4)$$

which relate an energy change (e.g. dG) to the ways in which that energy can change.

3.1. Constraints

Activation energy is a constraint in real systems, but in thermodynamics constraints must be mathematical variables, and so are state variables associated with ways in which a system can change its energy. Defined this way, all thermodynamic systems have at least two constraints, because they are always defined as being able to exchange energy with their environment by heat and one form of work (pressure–volume work), and one state variable must be assigned for each. For Gibbs energy these are temperature T and pressure P (Eq. (4)), for internal energy U they are entropy S and volume V, and so on for each of the thermodynamic potentials and their associated fundamental equations. If there are additional ways of changing the system energy such as an internal chemical reaction (or gravity, tensile force, electrochemical cells, etc.) there will be an additional constraint variable for each. Systems achieve equilibrium subject to the imposed constraints (Reiss, 1965, p. 13–14; Pippard, 1966, p. 104–108) and *stable* equilibrium is the state of the system at equilibrium having the minimum two constraints. Additional constraints prevent the system from achieving stable equilibrium, and

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[1] Activation energy as well as the enthalpy and entropy of activation are variables in transition state theory and reaction kinetics, but these quantities are not relevant to the present discussion.
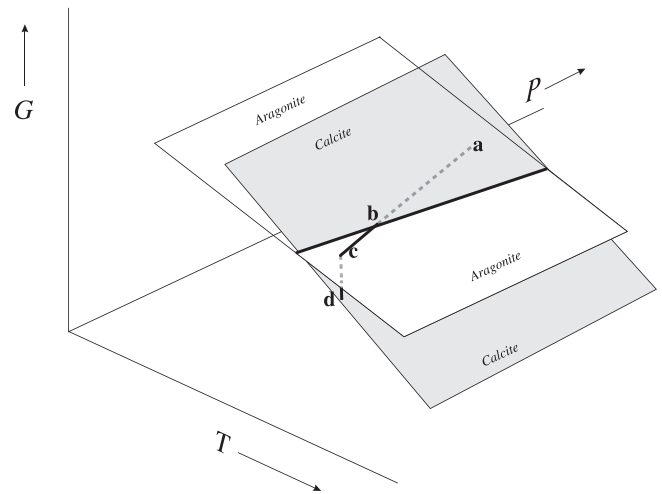

Fig. 1. Schematic *GTP* surfaces for calcite and aragonite. Aragonite is the stable phase as P decreases from a to b, where $\Delta_r G = 0$. A kinetic barrier prevents the reaction to form calcite at b. Aragonite continues as a metastable phase to c with $\Delta_r G$ increasing. At c $\Delta_r G$ is sufficiently great to overcome the kinetic barrier and the reaction to calcite c → d takes place. The change in P and/or T from b to c is called overstepping.

result in systems at *metastable equilibrium*. Removal of such a constraint results in a spontaneous process leading to a more stable equilibrium state (Weinreich, 1968, p. 137; Callen, 1985, p. 26; Jaynes, 1992, p. 20).

3.2. A constraint in an isolated system

The entropy paradox refers to isolated or constant U, V systems which are rare to non-existent in nature. Nevertheless, the implications of the paradox apply to irreversible processes in all thermodynamic systems, including the constant T, P systems more commonly used. To illustrate the paradox we consider an internal volume change rather than a chemical reaction in the simple system shown in Fig. 2. If there is only one additional constraint which is also continuously variable, entropy will be a function of three variables (the two initial independent variables U and V plus the additional constraint variable) having a maximum with $dS_{U,V} = 0$. The system consists of an ideal gas in a container impermeable to energy transfer and perfectly rigid (an isolated system) and partitioned by a movable piston which can be locked in place, giving one example of an internal or thermodynamic constraint. The piston is impermeable to gas but conducts heat, so the two sides are at the same temperature. Entropy is defined such that it is maximized in such a system when there is no internal constraint; i.e., when the piston is unlocked and free to move. With equal amounts of gas on both sides, this will be in the middle of the cylinder, as shown, and a plot of the entropy of an ideal gas vs. a constraint variable representing the position of the piston (such as $V_1/(V_1 + V_2)$) will be symmetrical and convex upward as in Fig. 3. Processes represented by such curves consist of a continuous succession of metastable equilibrium states, and have been called *quasistatic*. They must be equilibrium states because if the system was not in equilibrium it's entropy could not be plotted on such a diagram. Several other more realistic but less simple cases are discussed by Reiss (1965).

3.3. A constraint variable in a reacting system

Although there is no constraint variable for activation energy as such, there is one for an irreversible process which proceeds when this barrier is overcome. This irreversible process causes an energy (and/or entropy) change within the system, so we need another term on the right side of Eq. (4). Ever since DeDonder (1920, 1927) introduced the extent of reaction variable (ξ) this third term has been identified as $-\mathcal{A} \, d\xi$, where $\mathcal{A}$ is the affinity and ξ is the new state variable, an