Exercise 4. Write the Gibbs equation for: (a) A simple magnetic substance, (b) A simple electric substance, (c) A complex substance with appreciable compressible and surface work modes.

Exercise 5. When the Gibbs equation is applied to an isolated system ($dU = dV = dN = 0$), it predicts $dS = 0$. But the second law for an isolated system, eqn. IIIB-4, is $dS \geq 0$. Are these two statements in conflict? How can their difference be explained?

Although the Gibbs equation is our principal means to evaluate entropy change, it has no direct second law significance.[16] Second law significance is obtained when the entropy change for the system and the surroundings are substituted into eqn. IIIB-5 to determine ΔS_{univ}. This quantity, which is a measure of the irreversibility of a process, is called its *entropy "production"* (or just *production*).

It is helpful in the development of engineering judgement to recognize how production originates. If we substitute the intrinsic form of the first law, $dU = đQ + đW^i_{irr} + đW^i_{rev}$, into the Gibbs equation we obtain

$$dS = \frac{đQ + đW^i_{irr}}{T} \qquad \text{(IIIB-21)}$$

We have established the fact that irreversible work is positive semidefinite, $đW^i_{irr} \geq 0$ (Unit IB, Section III). Therefore, eqn. IIIB-21 can be expressed in the form

$$dS \geq \frac{đQ}{T} \qquad \text{(IIIB-22)}$$

This expression, called the *Clausius inequality*, indicates a second law limitation imposed upon the system alone. When Clausius inequality is applied to a closed system undergoing an adiabatic process, we see that its entropy can only increase.

$$dS\big|_{ad} \geq 0 \qquad \text{(IIIB-23)}$$

Though this expression has the same form as eqn. IIIB-4, it is not restricted to isolated systems; work interactions are allowed.

Eqn. IIIB-23 is not a complete statement of the second law. It only describes the second law consequences for an adiabatic process. Each of our second law statements, eqns. IIIB-4, 5, 22, and 23 expresses a tendency for the entropy to increase. The student must remember that it is the entropy of the universe, not that of an interacting system that cannot decrease.

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[16] The Gibbs equation also provides a general link between measurable and unmeasurable properties. It is the basis for the development of the Maxwell Relations, Unit IVD.

Ans. 3. Initially the entire crystal was in equilibrium. The "pumping" process added energy to the lasing states causing a nonequilibrium condition in the crystal. As discussed above this requires irreversible work (or heat). Further evidence that this is the case is provided by the fact that the energy levels of the lasing states are not altered.