

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Thermodynamics of Materials

3.00 Fall 2000

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Exam 2: Friday November 17, 2000 (Solutions)

Exam Question 2.1

Read *carefully* and determine whether the following statements are true or false and indicate your thermodynamic reasoning. If you claim that a statement is false, you may state which of the laws of thermodynamics that it violates or you may employ a physical counter-example. If the statement is false, you may wish to amend the statement with a clarifying phrase that makes the statement true.

2-1-i A body in equilibrium and in thermal and mechanical contact with a reservoir at constant pressure and temperature will have the lowest possible value of Gibbs Free energy for that body.

True. It was demonstrated in class that a condition for equilibrium was that any virtual change of the total Gibbs free energy at constant P and T must be positive as a condition of equilibrium. The body could have a lower value of G at different pressures or temperatures, or if the equilibrium was not the absolute equilibrium at that T and P .

2-1-ii The entropy of a material can never decrease. False. The second law applies to a material and its surroundings. Water freezes into ice that has a lower entropy.

2-1-iii If two phases that are composed of the same kind of pure material are in equilibrium at constant pressure, then they must have the same value of Gibbs free energy.

Almost True. They would have the same value of Gibbs free energy if both phases have the same extent (i.e., number of moles). It would be correct to say that they have the same molar Gibbs free energy.

2-1-iv The internal energy of a system and its surroundings is not conserved during an irreversible process.

False. The first law says that the internal energy of a system is conserved for any process.

2-1-v Melting of a fixed amount of a pure material at constant pressure is an endothermic process when the entropy of a liquid is greater than the entropy of a solid.

True. $\Delta\bar{G} = 0 = \Delta\bar{H} - T\Delta\bar{S}$. Therefore $\Delta\bar{H}$ has the same sign as $\Delta\bar{S}$.

2-1-vi For a system composed C components with chemical potentials μ_i for the i -th component and N_i is the number of molecules of the i -th species, $\sum_{i=1}^C \mu_i N_i$ will always have its smallest possible value.

Approaches Truth. $G = \sum_{i=1}^C \mu_i N_i$ and G approaches its smallest value subject to constraints of fixed T and P as the system approaches equilibrium.

Exam Question 2.2

One mole of pure substance at constant pressure is observed to melt at T_m and boil at T_v . For a temperature range $T_{low} < T_m < T_v < T_{high}$ and constant pressure, sketch plots of the following (for molar quantities, draw curves for stable and unstable phases; label relevant points and curves):

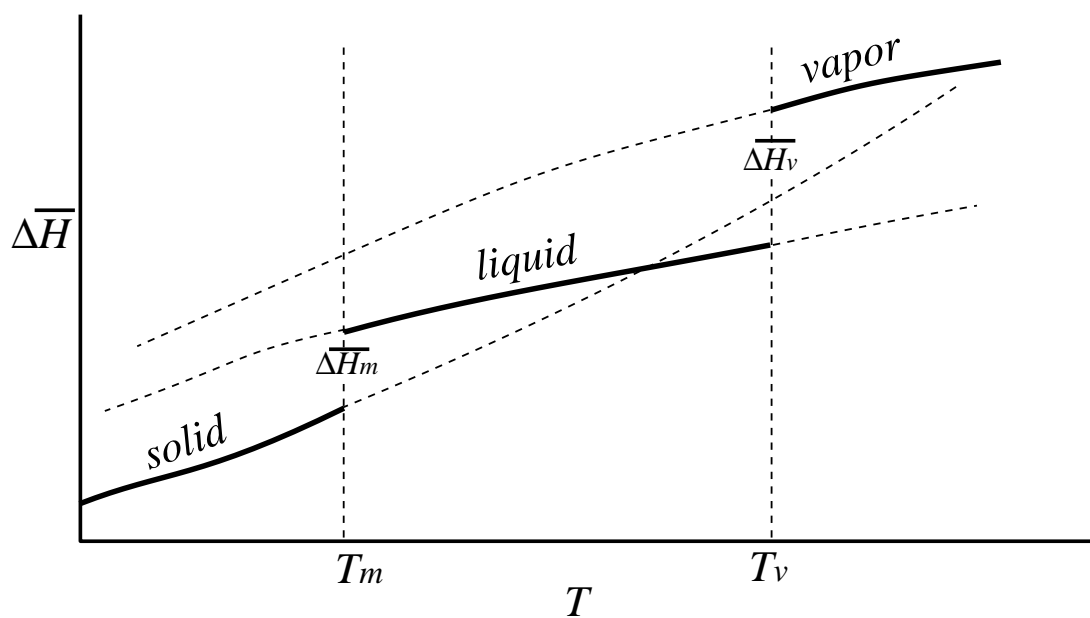


Figure 2-2-i: \bar{H} versus T .

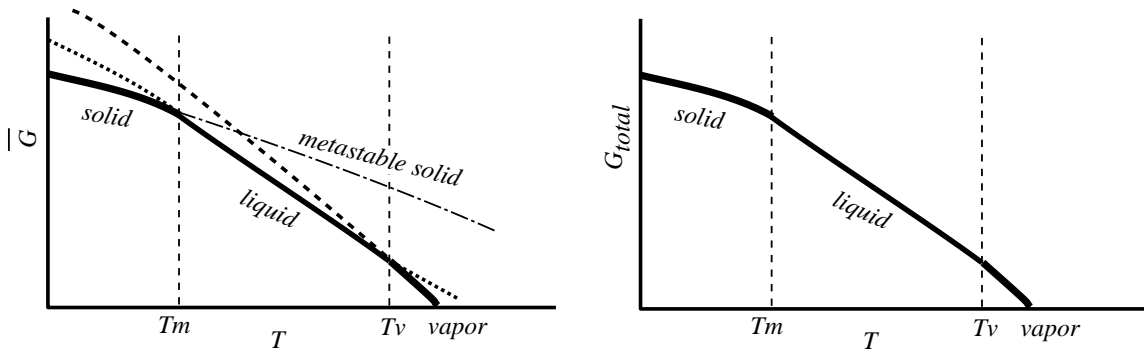


Figure 2-2-ii: G_{total} versus T and \bar{G} versus T .

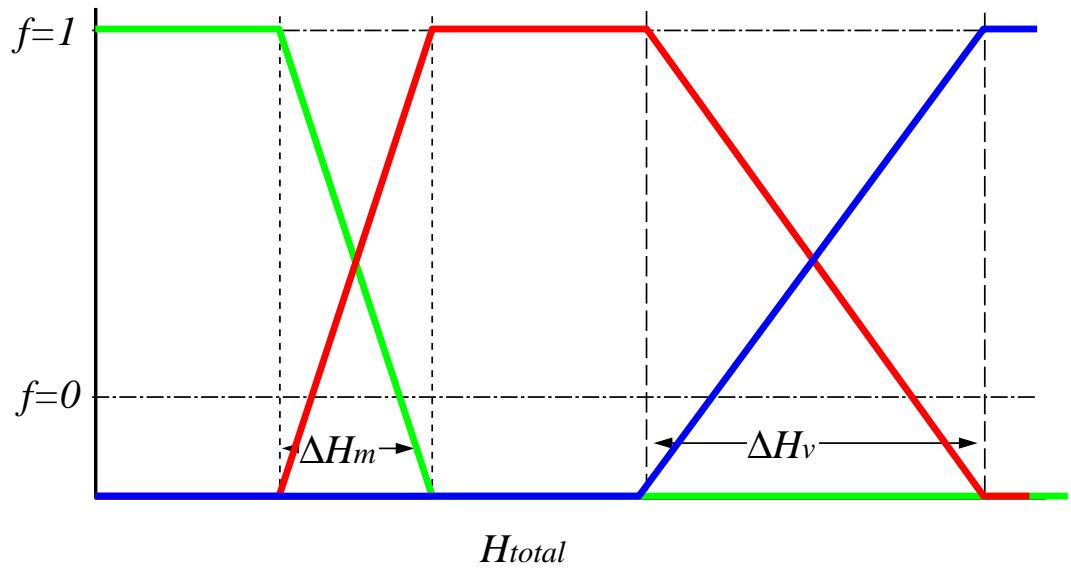


Figure 2-2-iii: Phase fractions versus H_{total} .

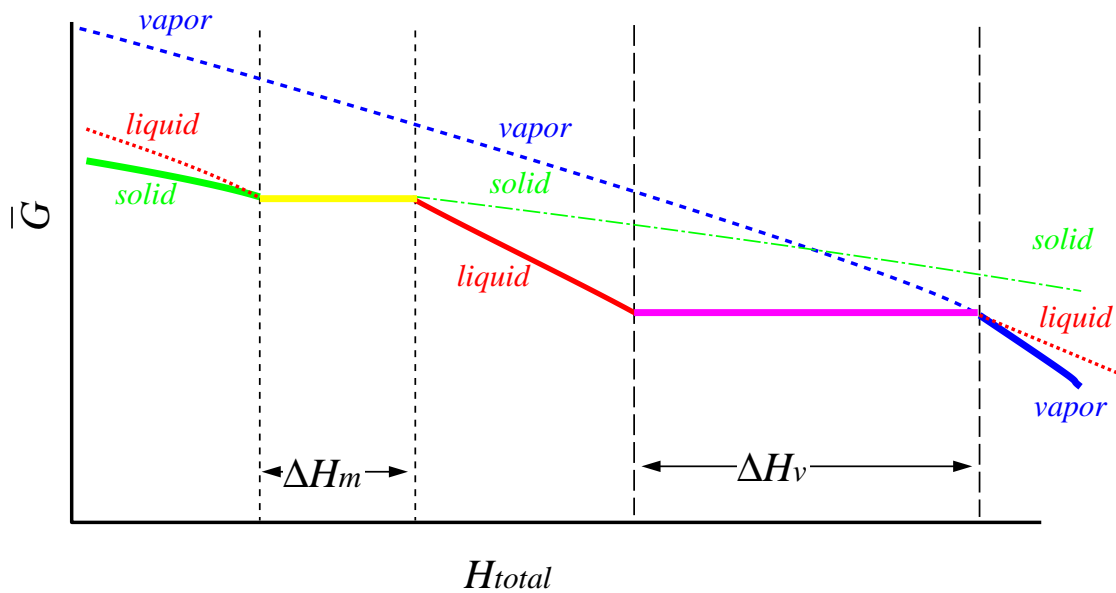


Figure 2-2-iv: \bar{G} versus H_{total} .

Exam Question 2.3

Calculate the change in: (1) the entropy of two moles of monatomic ideal gas, and (2) the entropy of the universe for the following processes:

2-3-i An isothermal free expansion ($P_{surroundings} = 0$) from an ideal gas volume of $V_{initial} = V_0$ to $V_{final} = 2.7182818V_0$ at $T = 300K$.

Entropy is a state function; therefore, only the initial and final states need to be known for its calculation. For an ideal gas, $dU = C_V dT$, therefore the ideal gas has no change in internal energy. Because, the ideal gas does no work on the surroundings and its internal energy is unchanged, there is no net exchange of heat with the surroundings: $\Delta S_{surr} = 0$ and $\Delta S_{univ} = \Delta S_{sys}$.

For the system, $C_V dT = T dS - P dV$. Because the process is isothermal,

$$\Delta S_{sys} = \int_{V_{initial}}^{V_{final}} \frac{PdV}{T} = \int_{V_0}^{2.7182818V_0} \frac{nRdV}{V} = 2R \log e = 2R$$

2-3-ii An isothermal and reversible expansion from an ideal gas volume of $V_{initial} = V_0$ to $V_{final} = 2.7182818V_0$ at $T = 300K$.

For a reversible process, $\Delta S_{univ} = 0$ and with the initial and final states being the same as above, $\Delta S_{sys} = 2R$.