

THERMODYNAMIC IDENTITY FOR GIBBS & HELMHOLTZ FREE ENERGIES

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*,
(Addison-Wesley, 2000) - Problems 5.8 - 5.10.

The thermodynamic identity for energy is

$$(1) \quad dU = T dS - P dV + \mu dN$$

With the definitions of Helmholtz and Gibbs free energies F and G and enthalpy H we can derive analogues to this identity for these other three energies.

The Helmholtz energy is

$$(2) \quad F = U - TS$$

Taking differentials, we get

$$(3) \quad dF = dU - T dS - S dT$$

$$(4) \quad = -S dT - P dV + \mu dN$$

For enthalpy, we get

$$(5) \quad H = U + PV$$

$$(6) \quad dH = dU + P dV + V dP$$

$$(7) \quad = T dS + V dP + \mu dN$$

Finally, for the Gibbs energy we have

$$(8) \quad G = U - TS + PV$$

$$(9) \quad dG = dU - T dS - S dT + P dV + V dP$$

$$(10) \quad = -S dT + V dP + \mu dN$$

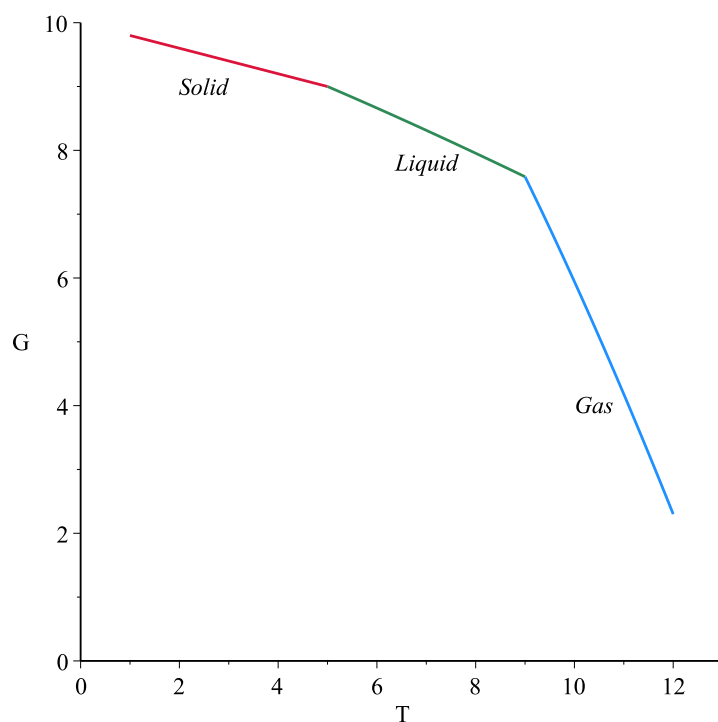
From the latter identity we can derive a few partial derivatives:

$$(11) \quad S = - \left(\frac{\partial G}{\partial T} \right)_{V,N}$$

$$(12) \quad V = \left(\frac{\partial G}{\partial P} \right)_{T,N}$$

$$(13) \quad \mu = \left(\frac{\partial G}{\partial N} \right)_{T,P}$$

From 11, we can get an idea of how G varies with temperature for a pure substance as it starts from a solid, then melts to a liquid and finally boils to a gas. We expect the entropy to be lowest when the substance is a solid, then become larger when it's a liquid and finally to be largest when it's a gas. This is illustrated in the following plot (qualitative; don't pay any attention to the values on the axes).



Because of the minus sign, we therefore expect G to decrease with temperature, starting off with a fairly shallow slope in the solid phase (red), then changing to a steeper slope in the liquid phase (green) and finally to the steepest slope in the gas phase (blue). The various segments would probably not be straight lines, especially in the gas phase, since the entropy would tend to increase with temperature, so the curves in the liquid and gas phases would probably be concave downwards.

Over relatively small changes in the state variables, we can use 10 to estimate changes in G as we vary one of the variables, holding the others constant. For example, if we start with a mole of water at 25° C and 1 bar and increase its temperature to 30° C at constant pressure (and constant molecule number N), the change in G is approximately (using the value for S from Schroeder's book):

$$(14) \quad \Delta G \approx -S \Delta T$$

$$(15) \quad = -69.91 \times 5$$

$$(16) \quad = -349.55 \text{ J}$$

If we want G to remain constant, we can compensate the decrease by increasing the pressure so that

$$(17) \quad V \Delta P = S \Delta T$$

One mole of water has a volume of around 18 ml, so the required pressure change is

$$(18) \quad \Delta P = \frac{349.55 \text{ J}}{18 \times 10^{-6} \text{ m}^3} = 1.94 \times 10^7 \text{ N m}^{-2} = 194 \text{ bar}$$

Thus we'd need to increase the pressure by a large amount. These are only rough estimates, since we're assuming that the behaviour of the variables is linear over the changes in T and P .

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