

Quick review of classical thermodynamics

Chemistry 422/522, Spring 2021

1 First and second laws

Someone (but I can't remember who!) said "thermodynamics is two laws and a little calculus". Please read Chapters I and II in the Slater handout, and look at Chapters 3, 6, and 10 in the Dill and Bromberg book. Let's start with Eq. 2.1 in the Slater book:

$$dU = dQ - dW \quad (1)$$

But look at p. 49 in Dill & Bromberg:

$$\Delta U = q + w \quad (2)$$

The change in sign has to do with how "work" is defined. We'll stick with Slater's convention for right now. We can easily get to this:

$$\Delta u = U_2 - U_1 = \int_1^2 dQ - \int_1^2 dW \quad \int_1^2 du = u_2 - u_1 \quad (3)$$

As I hope you know, neither of the terms on the RHS are uniquely defined, but rather are *path-dependent*. As experience with steam engines in the 19th century established clearly, heat and work can be interchanged. But the **first law** states that $\Delta U = 0$ for an isolated system, and that U is a state function. The **second law** states that dQ/T is also a state function (independent of path), and there is a quantity, entropy, that is related to it:

$$dS \geq dQ/T \Rightarrow TdS \geq dU + dW \Rightarrow dW \leq TdS - dU \quad (4)$$

(There is actually a **zeroth law** that posits the existence of equilibrium states characterized by a temperature.)

2 Equations of state

Following Chap. II of Slater, we will restrict "work" (for now) to pressure-volume work: $dW = pdV$ note that this has the form of a force times a displacement, as expected. Then we have five variables that characterize an equilibrium system: p, V, T, U and S . Two of these (p, T) are *intensive*, the other three are *extensive*. Derivatives with respect to the intensive variables often represent measurable quantities. For example, the isothermal compressibility is defined as

$$-\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (5)$$

A related quantity is the *adiabatic compressibility*; here "adiabatic" means "no heat flow", so that $dQ = 0 = dS$ where the second equality applies to reversible processes. Hence this quantity is:

$$-\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S \quad (6)$$

Changes with respect to temperature are also ubiquitous. One of the most common is to look at the change in Q as a function of temperature, which is a *heat capacity*. At constant volume, there is no work, so $dQ = dU$.

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V = \left(\frac{\partial Q}{\partial T} \right)_V \equiv T \left(\frac{\partial S}{\partial T} \right)_V \quad (7)$$

where, again, the final equality is for reversible processes. At constant pressure, $TdS = dU + pdV$, so the heat capacity becomes:

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p = \left(\frac{\partial(U + pV)}{\partial T} \right)_p \equiv \left(\frac{\partial H}{\partial T} \right)_p \quad (8)$$

So, at constant pressure, the change in enthalpy is equal to the heat absorbed.

3 Free energies

See p. 21 in Slater for a discussion of why we can think of TS and the "energy bound as heat". One way to see this is to define $A = U - TS$. Then:

$$d(ab) = a db + b da \quad dA = dU - TdS - SdT \leq -dW - SdT \quad (9)$$

where the inequality comes from the second law, Eq. 4. Hence, at constant temperature, $dW \leq -dA$: the work done is always less than or equal to the decrease in Helmholtz free energy. At equilibrium, we can write:

$$dA = -pdV - SdT \Rightarrow \left(\frac{\partial A}{\partial V} \right)_T = -p \quad \text{and} \quad \left(\frac{\partial A}{\partial T} \right)_V = -S \quad (10)$$

It is often more convenient to use pressure and temperature, rather than volume and temperature, as the independent variables. Then it is useful to define $G = H - TS$ as the free energy. Please read carefully pp. 22-23 of Slater if you are not familiar with this transformation. The equivalent of the previous equation becomes:

$$dG = Vdp - SdT \Rightarrow \left(\frac{\partial G}{\partial p} \right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T} \right)_p = -S \quad (11)$$

(An aside: in condensed phases at ordinary pressures, ΔV is small, since liquids are nearly incompressible. So little pV work is done, and we can write that $\Delta G \approx \Delta A$ and $\Delta H \approx \Delta U$.)

4 Fundamental and derived quantities

So far, we have been dealing with systems with a given number of particles. The extension to mixtures with variable number of particles introduces the *chemical potential*:

$$dG = Vdp - SdT + \sum_i \mu_i dn_i \quad \text{and} \quad dU = TdS - pdV + \sum_i \mu_i dn_i \quad (12)$$

dn_i = change in number of mols of component

$$\underline{N} = (n_1, n_2, n_3, \dots)$$

Please read the discussion on pp. 95-97 of Dill and Bromberg. The Y consider the "fundamental" equations of state as $S(U, V, N)$ and $U(S, V, N)$. Note that these are only functions of extensive variables. For $U(S, V, N)$ we must have:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \sum_i \left(\frac{\partial U}{\partial n_i}\right)_{S,V} dn_i \quad (13)$$

Combining the last two equations, we can treat the following as definitions of the intensive variables:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}; \quad p = -\left(\frac{\partial U}{\partial V}\right)_{S,N}; \quad \mu_i = \sum_i \left(\frac{\partial U}{\partial n_i}\right)_{S,V} \quad (14)$$

look at Table 8.1 p 140

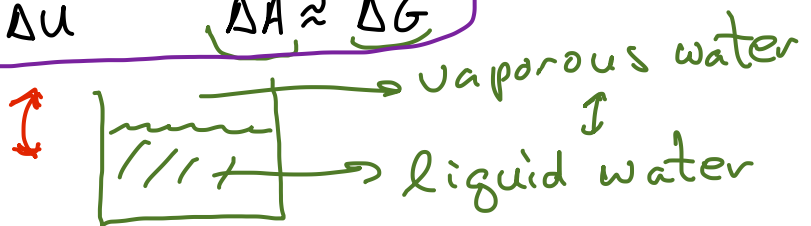
fundamental	U, S	U is heat at const V
derived	$H = U + pV$	H " " P
Helmholtz	$F \equiv A = U - TS$	A is max work const V
Gibbs	$G = H - TS$	G " P

aside in condensed phases, generally ΔU is small
water are ^{nearly} incompressible

$$\Delta H \approx \Delta U \quad \Delta A \approx \Delta G$$

at equilibrium

caveat!
 $\hookrightarrow \mu_{\text{vapor}} = \mu_{\text{liquid}}$



most experiments (open to air) have such an equilibrium, and the vapor is not incompressible.