

On activities

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This document was inspired by curious questions of Ríša Veselý.

Thermodynamics is this funny theory that gives us equations that we know work and can easily experimentally test that they do, but we arrive at them via multiple levels of abstraction using many confusing concepts.

The internal energy U is well defined by the first law of thermodynamics:

$$dU = \delta q + \delta w \quad (1)$$

However, this defines unambiguously only the change of internal energy between states, but not the energy zero, which we can set arbitrarily.

The second and third law then define entropy. The second law its change between states and the third law its zero.

$$dS = \frac{\delta q_{rev}}{T} \quad (2)$$

$$\lim_{T \rightarrow 0} S = 0, \text{ for an ideal crystal} \quad (3)$$

Having defined these, we can rigorously define enthalpy, the Gibbs energy and the Helmholtz energy, where the arbitrary zero of the internal energy has propagated to all three quantities.

$$H = U + pV \quad (4)$$

$$G = H - TS \quad (5)$$

$$A = U - TS \quad (6)$$

Having defined these, we can define the chemical potential μ . In words, it is the change in free energy of the system upon addition of one particle. A slight

problem with including this definition in our equation is that the number of particles is not a continuous variable, but for macroscopic systems it is typically taken to be well approximated by it. This changes the first law as follows

$$dU = \delta q + \delta w + \sum_i \mu_i dN_i. \quad (7)$$

This propagating through the definitions leads to the most commonly used formula

$$\mu_i = \left(\frac{\partial G}{\partial N} \right)_{T, P, N_{j \neq i}}. \quad (8)$$

The activity of species i is then defined by

$$\mu_i \equiv \mu_i^\circ + RT \ln a_i, \quad (9)$$

where μ_i is the chemical potential of species i and μ_i° is the corresponding standard chemical potential (i.e. the chemical potential at standard conditions). Since both chemical potentials are well defined, it means that activity is whatever number that needs to be in the equation to make it true. This is not the way it is presented in textbooks, because it looks like an extremely arbitrary definition (which it is). However, activity is actually very useful. Textbooks then typically continue to say: The activity can be calculated by

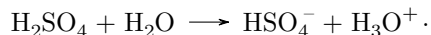
$$a_i \approx \frac{c_i}{c^\circ} \approx \frac{p_i}{p^\circ} \approx \frac{x_i}{x^\circ}, \quad (10)$$

where c is concentration, p is pressure and x is molar fraction. The typical values for their standards are 1 mol dm^{-3} , 1 bar and 1 respectively. For solutes we use concentrations, for gasses pressures and for pure phases and simple mixtures mole fractions. If the book is more careful, they use

$$a_i = \gamma_{ci} \frac{c_i}{c^\circ} = \gamma_{pi} \frac{p_i}{p^\circ} = \gamma_{xi} \frac{x_i}{x^\circ}, \quad (11)$$

where γ 's are the activity coefficients, which most of the time (i.e. in the textbook examples) are close to unity. These coefficients are the kind of “fudge” constants, which are there just to make the original equation work, where it should not. This can be seen as justified as long as they do not deviate from one too much and are approximately constant over the range of conditions that we are considering.

This is the “Hang on a second ...” moment. If we take for example the reaction



Considering the activity as we increase the concentration of the sulfuric acid, we should go from a dilute solution increasing the concentration until we have sulfuric acid as the solvent and water as the solute. We are also told that

solvents, which are assumed to be a pure phase, have the activity equal to one (mole fraction is basically one). However, looking at the equations we got as we are increasing the concentration, the activity at the beginning increases linearly with concentration and then we expect some deviation from this due to the activity coefficient. At 2 or 3 M solution, we have probably deviated slightly, but by the time we reach 18.7 M, the activity must be one again, since it is pure sulfuric acid. And just before that point, it should be below one as the molar fraction is below one. The activity should be a respectable thermodynamic quantity and not a roller-coaster that goes up and down like that! When increasing the concentration of sulfuric acid, there are no regimes of interactions that would suddenly change, which would give physical foundation to such behaviour.

The devil is of course in the detail. What may have worried us already in the preceding reasoning is that activity depends on this arbitrary standard concentration and pressure. This tells us that the activity is directly connected with our choice of standard states. However, the chemical potential, as a well defined thermodynamic quantity, has to be the same regardless of what our standard states are (assuming we have fixed the arbitrary zero consistently). Let me write out the equations again in a more suggestive way.

$$\mu_i = \mu_i(c^\circ) + RT \ln a_i^c = \mu_i(c^\circ) + RT \ln \left(\gamma_{ci} \frac{c_i}{c^\circ} \right) = \quad (12)$$

$$= \mu_i(p^\circ) + RT \ln a_i^p = \mu_i(p^\circ) + RT \ln \left(\gamma_{pi} \frac{p_i}{p^\circ} \right) = \quad (13)$$

$$= \mu_i(x^\circ) + RT \ln a_i^x = \mu_i(x^\circ) + RT \ln \left(\gamma_{xi} \frac{x_i}{x^\circ} \right) \quad (14)$$

Note that there is only one chemical potential, which can be expressed using different types of activities *and* different standard chemical potentials. This means that equation 11 is plainly wrong. Those are definitions of activities relating to completely different standard states and their numerical values can be equal only by coincidence.

Thus if we imagine the sulfuric acid example, the chemical potential of the sulfuric acid increases monotonically from zero concentration to pure acid. Assuming that the equations hold and that the activity coefficients are sufficiently constant, there will be two regimes, one where the potential varies linearly with the logarithm of concentration and one where it varies linearly with the logarithm of the molar fraction. We may also expect some transitional regime in between. It is possible to describe the chemical potential throughout using just the concentration or just the mole fraction equation, not changing the reference standard state mid way. However, we would expect the concentration activity coefficient to deviate from one at high concentrations and the mole fraction activity coefficient to deviate from one for dilute solutions. It would be interesting

to calculate the exact variation, if experimental data are available.

In most experimental setups and practically all textbook problems the change of the reference state is not required. However, I find that all relevant texts that I have seen do not emphasise sufficiently the existence of different activities and their related standard chemical potentials making it confusing for the students. I hope that this document has helped you to clarify these concepts.