

4: Some Practical Consequences

In the foregoing, we have shown how entropy completes macroscopic thermodynamics and connects it to microscopic statistics. While this is highly satisfying, it is the predictive power of theory that is of practical significance. Working our way backwards through the relationships in the previous two chapters, we see that if we can enumerate the microstates of a system and propose energies and volumes for each of them, then we can calculate the equilibrium probabilities of these states and the averages that correspond to macroscopic properties at equilibrium. Thus, the statistical thermodynamics takes us from a microscopic model to macroscopic predictions, with increasing confidence as models are validated by experiments that test their predictions. Let's consider some examples.

Heat capacities

Quantum mechanics allows us to calculate the energies of molecules. At ordinary temperatures, only the ground electronic state is significantly populated because even the first excitation requires an energy $\gg kT$. However, rotational, vibrational and translational excited states are all populated at ordinary temperatures and it turns out that the spacings in their energy ladders have different characteristic patterns. As a result, the contributions to the constant volume heat capacity are $k/2$ for each translational or rotational mode and k for each vibrational mode. This prediction comports with several interesting experimental observations.

- All molecules have three translational modes (one for each Cartesian coordinate), but linear molecules have one less rotational mode and one more vibrational mode than nonlinear molecules with the same number of atoms. This difference agrees with the experimentally observed differences in gas phase heat capacities of linear vs. non-linear molecules.
- A lattice solid can be viewed as a single very large molecule of N atoms, where N is of the order 10^{23} . Since N atoms have a total of $3N$ degrees of freedom, the three translational and three rotational modes are vastly outnumbered by the $(3N - 6) \sim 3N$ vibrational modes. This agrees with the experimentally observed heat capacity of $3k$ per atom for lattice solids.
- Liquid water has the $3k$ per atom heat capacity typical of lattice solids. This attests to the importance of its three-dimensional hydrogen bonding network.
- Excitations are frozen out with decreasing temperature, as expected according to the Boltzmann distribution. First to go are the electronic excitations (already at ordinary temperatures in most cases), then the vibrational excitations (in the infrared range of energies), and then the rotational excitations (in the microwave range of energies). At each of these stages, the corresponding contributions to the constant volume heat capacity also disappear as predicted.

Gas phase chemical equilibria

The reactants and products of a chemical reaction are different arrangements of the same atoms. Using quantum mechanics, we can calculate energies for the electronic, rotational, vibrational and translational states of each, and then use these to determine the temperature and pressure dependence of the relative probabilities of products and reactants. This yields an equilibrium reaction quotient (generally known as the "equilibrium constant"). While the form of the equilibrium constant can be derived from the macroscopic picture of mass action, the value of the equilibrium constant is predicted from the microscopic picture by statistical thermodynamics.

Phase behavior of pure substances

All uncharged molecules attract one another. Even if they have no hydrogen bonding capability and have no permanent dipole moment, they have fluctuating dipole moments due to electron motion. The tendency of these fluctuations to become coordinated in neighboring molecules results in intermolecular attractions, known as "London dispersion forces". As a result, only small molecules (i.e., those with few electrons) occur as gases at ordinary temperatures and pressures. As expected, the phase behavior follows a pattern dictated by trade-offs between energy, volume and entropy. At low temperature, where entropy is unimportant, the lowest energy phase prevails at low pressure and the lowest volume phase prevails at high pressure. Either way, this is a condensed phase. With increasing temperature, higher entropy becomes important and the gas phase eventually prevails. For a given pressure, this transition occurs at the temperature where the free energy of the gas phase dips below that of the condensed phase. Both of these free energies can be calculated from a model of intermolecular attractions in the condensed phase vs. the absence of intermolecular interactions in the gas phase. For transitions between different condensed phases, modeling must consider how the details of molecular packing distinguish the intermolecular attractions in each phase.

Phase behavior of mixtures

Entropy always favors mixing and the energies of intermolecular interactions almost always favor demixing to some extent. The latter is because mixing involves replacing interactions between like neighbors with interactions between unlike neighbors and this often involves losing H-bond interactions or dipole-dipole interactions. As a result,

- Gases are always completely mixed because there are no intermolecular interactions.
- Lattice solids are generally nearly pure, due to packing constraints that optimize intermolecular interactions.
- The tradeoffs between entropy and energy play out primarily in the liquid phase. This is where we most commonly see phase separation. The difference in composition of the coexisting phases increases with the severity of the energy penalty for mixing. However, neither phase will ever be completely pure because the entropy that is sacrificed in removing minor component(s) in either phase gradually diverges.

Polymer swelling and collapse

Entropy favors polymer chains exploring all configurations that their lengths and open space allow. This will be countervailed by energy costs of bending. The balance will be influenced by the nature of the interactions between polymer units and solvent, with swelling in a good solvent (one where hetero interactions are more favorable) and collapse in a bad solvent (one where hetero interactions are less favorable).

Elasticity

Configurational statistics also underlie the ability of polymeric materials to sustain very large deformations in reversible fashion. This can be demonstrated by a simple experiment with an ordinary rubber band. When a weight is suspended from the rubber band, the equilibrium length reflects a compromise between the gravitational potential energy of the weight, which tends to stretch the rubber band, and the configurational entropy of the polymers, which works against the distortion. Accordingly, the rubber band shortens with increasing temperatures, where the influence of entropy is greater.

Thermal expansion

For most materials, higher temperatures lead to expansion because higher volume states are usually higher entropy states. Moreover, the trade-off against energy is such that the thermal expansion is typically greater for materials with weaker bonds. In the unusual cases where thermal expansion is negative, it is a sign of access to bonding arrangements with greater entropy at reduced volume. The most well-known case is that of water from 0°C to 4°C, at 1 atm. The anomalously high density of liquid water near freezing causes bodies of water to freeze from the top down which helps to protect aquatic life through the winter.

Liquid crystals

When molecules are elongated, they spontaneously align above a certain concentration. This would seem to violate the rule that spontaneous change occurs in the direction of increasing entropy. However, a close examination of the statistics shows that this is a case of "entropically-driven order": when elongated particles align at concentrations high enough to get in each other's way, it is because the gain in their translational freedom (both laterally and longitudinally) exceeds the loss in their orientational freedom.

Hydrophobicity

Liquid water is a very special substance due to its exceptional entropy. Not only are water molecules free to move as in any liquid, but their interactions with one another are highly labile. In roughly tetrahedral fashion, each oxygen can donate up to two hydrogen bonds to neighbors and accept up to two from others. Moreover, the protons can hop-scotch through the network, interconverting donated and accepted H-bonds as they go. Solutes interfere with this network's very high multiplicity of states. Therefore, the entropy of mixing solute and solvent is not enough for non-polar solutes to dissolve to significant extent in water. On the other hand, for polar solutes, energetically favorable interactions with water can tip the balance to allow greater solubility and, in some cases, even full miscibility.

The surface charge of neat water

Water is amphiprotic and forms both hydroxide, by loss of a proton, and hydronium, by gain of a proton. None of these three species can form as many hydrogen bonds at the surface as in the bulk. However, when a surface water molecule is exchanged with a hydroxide from the bulk, there is a net gain in hydrogen bonding. As a result, hydroxide prefers residence at the surface to residence in the bulk. On the other hand, when a surface molecule is exchanged with a hydronium from the bulk, there is a net loss of hydrogen bonds and hydronium prefers residence in the bulk to residence at the surface. This behavior is manifest in the more

than century old observation that the mist formed by shearing the surface of water (e.g., by gravity in water falls or by wind over water bodies) is negatively charged. In effect, mechanical energy is being converted into electrical energy by separation of the negative surface charge from the bulk positive charge. Recently interest in this phenomenon has evolved from simple curiosity to schemes for harvesting the energy stored in water mists.

Chemical kinetics

Given its focus on equilibrium states, it would seem that thermodynamics has nothing to say about dynamics. However, this turns out not to be the case. In particular, statistical thermodynamics can predict the rates of chemical reactions. Just as we can use quantum mechanics to calculate energies for reactants and products, we can also use quantum mechanics to calculate energies for other configurations of the same collection of atoms. The resulting energy landscape maps the energy barrier between the reactants and products. The lowest region on this barrier (analogous to a pass in a mountain range) is called the "transition state" because it has the greatest chance of being populated according to the Boltzmann probability distribution and, consequently, the greatest chance of leading to a crossing from reactant to product. Given occupancy of the transition state, how long does the crossing take? A reasonable estimate is the period of the molecular vibration that corresponds to the shift from the reactant side of the barrier to the product side. The resulting prediction of the reaction rate is the product of the probability that the transition state is occupied and the frequency of the vibration that crosses the barrier.

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