The Entropy of a Substance at a Temperature, T

The entropy of a substance at any temperature T is not complex or mysterious. It is simply a measure of the total amount of energy that had to be dispersed within the substance (from the surroundings) from 0 K to T, incrementally and reversibly and divided by T for each increment, so the substance could exist as a solid or (with additional reversible energy input for breaking intermolecular bonds in phase changes) as a liquid or as a gas at the designated temperature. Because the heat capacity at a given temperature is the energy dispersed in a substance per unit temperature, integration from 0 K to T of $C_p/T \, dT$ (+ q/T for any phase change) yields the total entropy. This result, of course, is equivalent to the area under the curve to T in Figure 5.

![Figure 5: The $C_p/T$ vs. $T$ from 0 K for a substance. The area under the curve (plus q/T at any phase change) is the entropy of the substance at $T$.](image)

Phase Change: Fusion and Vaporization

To change a solid to a liquid at its melting point requires large amounts of energy to be dispersed from the warmer surroundings to the solid for breaking the intermolecular bonds to the degree required for existence of the liquid at the fusion temperature. (“To the degree required” has special significance in the melting of ice. Many, but not all of the hydrogen bonds in crystalline ice are broken. The rigid tetrahedral structure is no longer present in liquid water but the presence of a large number of hydrogen bonds is shown by the greater density of water than ice due to the even more compact hydrogen-bonded clusters of H$_2$O.) Quantitatively, the entropy increase in this isothermal dispersal of energy from the surroundings is $\Delta H_{\text{Fusion}} / T$. Because melting involves bond-breaking, it is an entropy increase in the potential energy of the substance involved. (This potential energy remains unchanged in a substance throughout heating, expansion, mixing, subsequent phase change to a vapor, or mixing. Of course, it is released when the temperature of the system drops below the freezing/melting point). The process is isothermal, and therefore there is no energy transferred to the system to increase motional energy. However, a change in the motional energy — not an increase in the quantity of energy — occurs from the transfer of vibrational energy in the ice crystal to the liquid. When the liquid forms, there is rapid breaking of hydrogen bonds (trillionths of a second) and forming new ones with adjacent molecules.
This might be compared to a fantastically huge dance in which the individual participants don’t move very far (takes a water molecule >12 hours to move a cm at 298K) but they are holding hands and then releasing to grab new partners far more frequently than billions of times a second. Thus, that previous motional energy of intermolecular vibration that was in the crystal is now distributed among a far greater number of new translational energy levels, and that means that there are many more accessible microstates than in the solid. Similarly, a liquid at its vaporization temperature has the same energy as its gas molecules. (All of the enthalpy of vaporization is needed to break intermolecular bonds in the liquid.) However in the case of liquid to vapor, there is a huge expansion (a thousand times increase) in volume. Therefore, this means closer energy levels, far more than were available for the motional energy in the liquid — and a greatly increased number of microstates for the vapor.

The Expansion of a Gas Into a Vacuum. The Mixing of Ideal Fluids. Dissolving solutes.

The entropy effects in gas expansion into a vacuum, as described previously, are qualitatively similar to gases mixing. From a macro viewpoint, the initial energy of each constituent becomes more dispersed in the new larger volume provided by the combined volumes of the components. Then, on a molecular basis, because the density (closeness) of energy levels increases in the larger volume, and therefore there is greater dispersal of the molecular energies on those additional levels, there are more possible arrangements (more microstates) for the mixture than for the individual constituents. Thus, the mixing process for gases is actually a spontaneous process due to an increase in volume. The entropy increases (6). Meyer vigorously pointed toward this same statement in "the spontaneity of processes generally described as "mixing", that is, combination of two different gases initially each at pressure, \( p \), and finally at total pressure, \( p \), has absolutely nothing to do with the mixing itself of either" (7).

The same cause — of volume increase of the system resulting in a greater density of energy levels — obviously cannot apply to liquids in which there is little or no volume increase when they are mixed. However, as Craig has well said, "The "entropy of mixing" might better be called the "entropy of dilution" (8b). By this one could mean that the molecules of either constituent in the mixture become to some degree separated from one another and thus their energy levels become closer together by an amount determined by the amount of the other constituent that is added. Whether or not this is true, ‘configurational entropy’ is the designation in statistical mechanics for considering entropy change when two or more substances are mixed to form a solution. The model uses combinatorial methods to determine the number of possible “cells” (that are identified as microstates, and thus each must correspond to one accessible arrangement of the energies of the substances involved). This number is shown to depend on the mole fractions of each component in the final solution and thus the entropy is found to be: \( \Delta S = - R \left( n_1 \ln X_1 + n_2 \ln X_2 \right) \) with \( n_1 \) and \( n_2 \) the moles of pure solute and solvent, and \( X_1 \) and \( X_2 \) the mole fractions of solute and solvent (8a, 9).

In general chemistry texts, configurational entropy is called ‘positional entropy’ and is contrasted to the classic entropy of Clausius that is then called ‘thermal entropy’. The definition of Clausius is fundamental; positional entropy is derivative in that its conclusions can be derived from thermal entropy concepts/procedures, but the reverse is not possible. Most important is the fact that positional entropy in texts often is treated as just that: the positions of molecules in space determine the entropy of the system, as though their locations — totally divorced from any motion or any energy considerations — were causal in entropy change. This is misleading. Any count of ‘positions in space’ or of ‘cells’ implicitly includes the fact that molecules being counted are particles with energy. Although the initial energy of a system is unchanged when it increases in volume or when constituents are mixed to form it, that energy is more dispersed, less
localized after the processes of expansion or of mixing. Entropy increase always involves an increase in energy dispersal at a specific temperature.

Colligative Properties

"Escaping tendency" or chemical potentials or graphs that are complex to a beginner are often used to explain the freezing point depression and boiling point elevation of solutions. These topics can be far more clearly explained by first describing that an entropy increase occurs when a non-volatile solute is added to a solvent — the solvent's motional energy becomes more dispersed compared to the pure solvent, just as it does when any non-identical liquids are mixed. (This is the fundamental basis for a solvent's decreased "escaping tendency" when it is in a solution. If the motional energy of the solvent in a solution is less localized, more spread out, the solvent less tends to "escape" from the liquid state to become a solid when cooled or a vapor when heated.)

Considering the most common example of aqueous solutions of salts: Because of its greater entropy in a solution (i.e., its energy more 'spread out' at 273.15 K and less tending to have its molecules 'line up' and give out that energy in forming bonds of solid ice), liquid water containing a solute that is insoluble in ice is not ready for equilibrium with solid ice at 273.15 K. Somehow, the more-dispersed energy in the water of the solution must be decreased for the water to change to ice. But that is easy, conceptually — all that has to be done is to cool the solution below 273 K because, contrary to making molecules move more rapidly and spread their energy when heated, cooling a pure liquid or a solution obviously will make them move more slowly and their motional energy become less spread out, more like the energy in crystalline ice. Interestingly, the heat capacity of water of an aqueous solution (75 J/mol) is about twice that of ice (38 J/mol). That means that when the temperature of the surroundings decrease by one degree, the solution disperses much more energy to the surroundings than the ice — and the motional energy of water and any possible ice becomes closer. Therefore, when the temperature decreases a degree or so (and finally to −1.86 C/kg.mol!), the solution's higher entropy has rapidly decreased to be in thermodynamic equilibrium with ice and the surroundings and freezing can begin. As energy (the enthalpy of fusion) continues to be dispersed to the cold surroundings, the liquid water freezes.

Of course, the preceding explanation could have been framed in terms of entropy change or numbers of microstates, but keeping the focus on what is happening to molecular motion, on energy and its dispersal is primary rather than derivative.

The elevation of boiling points of solutions having a non-volatile solute is as readily rationalized as is freezing point depression. The more dispersed energy (and greater entropy) of a solvent in the solution means that the expected thermodynamic equilibrium (the equivalence of the solvent's vapor pressure at the normal boiling point with atmospheric pressure) cannot occur at that boiling point. For example, the energy in water in a solution at 373 K is more widely dispersed due to the increased number of microstates for a solution than for pure water at 373 K. Therefore, water molecules in a solution less tend to leave the solution for the vapor phase than from pure water. Energy must be transferred from the surroundings to an aqueous solution to increase its energy content, thereby compensating for the greater dispersion of the water's energy due to its being in a solution, and to allow water molecules to escape readily to the surroundings. (More academically, “to raise the vapor pressure of the water in the solution”.) As energy is dispersed to the solution from the surroundings and the temperature rises above 373 K, at some point a new equilibrium temperature for phase transition is reached. The water then boils because the greater vapor pressure of the water in the
solution with its increased motional energy now equals the atmospheric pressure.

Osmosis

Although the hardware system of osmosis in the chemistry laboratory and in industry is unique, the process that occurs in it is merely a special case of the mixing of a solvent with a solution — 'special' because of the existence of such marvels as semi-permeable membranes through which a solvent can pass but a solute cannot. As would be deduced from the discussion about mixing two liquids or mixing a solid solute and a liquid, the solvent in a solution has a greater entropy than a sample of pure solvent. Its energy is more dispersed in the solution. Thus, if there is a semi-permeable membrane between a solution made with a particular solvent and some pure solvent, the solvent will spontaneously move through the membrane to the solution because its energy becomes more dispersed in the solution and thus, its entropy becomes increased if it mixes with the solution.

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