8.10: Thermodynamic Equilibrium

Those who have studied thermodynamics will be familiar with such elementary and easy concepts as entropy, enthalpy, Gibbs free energy, chemical potential, activity and fugacity, and will have no difficulty in grasping their meaning. Much more difficult to grasp, however, is the very difficult concept of temperature. I have vague memories of something called the Zeroth Law of Thermodynamics which, I seem to recall, went something like this: "If two bodies are in thermodynamic equilibrium with each other, and each is in thermodynamic equilibrium with a third, then all three bodies are at the same temperature." I understood that this was a law of great profundity, though I was never quite sure whether any part of the Universe could ever truly be in thermodynamic equilibrium and that the Universe would be a pretty dull place if it were. This section may or may not (more likely the latter) make the concept of temperature any easier.

Let us try to imagine a system consisting of a hot gas with a solid body suspended in it.

Let us imagine that we are somehow able to measure the distribution of the translational speeds of the molecules in the case, and the distribution is found to conform to a Maxwell-Boltzmann distribution with a root-mean-square speed V. We could then calculate the quantity $mV^2/(3k)$ and call this quantity T. We could call this quantity the *kinetic temperature* of the gas. We might, for example, say that the kinetic temperature of the gas is $300\ \mathrm{K}$. Some may think that it would be simpler merely to say how fast the molecules are moving. In any case, the *kinetic temperature* of the gas is merely a way of expressing what the root-mean-square speed of the molecules is.

Let us also imagine that we are able to determine how the molecules are partitioned among their numerous discrete energy levels. We may find that they are distributed according to the Boltzmann distribution with parameter T, and we could call that parameter the *excitation temperature*, which would then merely be a way of saying how fast or how slowly the occupation numbers of the levels fall off with energy.

We might also be able to determine the extent to which the atoms are ionized, and we could apply Saha's equation and hence define an *ionization temperature*.

Unless the molecules are single atoms, we might also be able to determine how the molecules are partitioned among their various vibrational levels or among their numerous rotational levels, and we could assign to these distributions a *vibrational temperature* and a *rotational temperature* respectfully.

If we look at the solid, it may be glowing with heat, and we may be able to determine how its exitance per unit wavelength interval varies with temperature, and we might observe that it conforms to Planck's radiation formula. We might be able to measure its total exitance, M. We could then pretend that it is a black body, and we could define $(M/\sigma)^{1/4}$, where σ is the StefanBoltzmann constant, as the *effective temperature*. Or we could note the wavelength at which the exitance per unit wavelength interval is greatest, and we could define W/λ_{max} as the *colour temperature* where W is Wien's constant..

Small wonder that "temperature" and "thermodynamic equilibrium" are such difficult concepts to grasp! However, I think it is fair to make the following statements: If the system is in thermodynamic equilibrium, then all of these various possible measures of "temperature" (kinetic, excitation, ionization, vibrational, rotational, effective, colour) are equal. If they are not equal, the system is not in thermodynamic equilibrium.