Thermodynamic Definitions

1. **Extensive Variable**: One that depends on the mass of the system; e.g., V, U, H, G, A, S etc. These variables are all homogeneous of degree one and additive. Mathematically, if U is extensive, U(kn) = kU(n) where k is a constant.
2. **Intensive Variable**: Variable that are independent of mass; e.g., T, P, μ, etc. Homogeneous of degree zero and not additive.
3. **System**: Object of interest in which a process may or may not occur. A 'simple system' is one whose variables of state are P, V and T and in which there are no fields, inhomogenarities.
4. **Surroundings**: That region of space external to the boundaries of the system and separated from the system by 'walls' which are either' adiabatic' or 'diathermal'. The surroundings consist of two discrete parts: 1) a heat reservoir of infinite capacity that can supply or abstract heat from the system if the walls are diathermal. 2) A work source at constant pressure.
5. **Closed System**: One that cannot exchange matter with the surroundings.
6. **Open System**: One that can exchange matter with the surroundings.
7. **Isolated System**: One that is adiabatic and closed with rigid wall so no work can be done, in short, one in which there can be no interaction with the surroundings.
8. **Adiabatic Wall**: One which permits a change in the state of the system by a change in the mechanical coordinates only, i.e., through the aegis of 'work'. Alternatively, a wall that does permit the flow of heat to or from the system. Examples, dewar flask or a polystyrene cup.
9. **Adiabatic Composite**: An adiabatically enclosed structure that contains both the system and its surroundings.
10. **Diathermal Wall**: One that does permit the flow of heat e.g., a copper wall.
11. **Heat Bath or Heat Reservoir**: A portion of the surroundings that can act as an accepter or donor of heat and which remains at constant temperature due to an infinite heat capacity. The reservoir also contains a work source with an infinite capacity, i.e., the mechanical variables of the reservoir do not change over time.
12. **Thermodynamic State**: The 'state' of the system is defined once the equilibrium values of the variables P, V, T etc. have been defined which allows the equilibrium properties to be calculated.
13. **Steady State Process**: A process occurring in a non-isolated system in which the intensive variables are time invariant, i.e., T, P, μ etc. but the extensive variables like S, U, H etc. do change over time. Systems that are in steady state are NOT in equilibrium. Most industrial processes are steady state operations.
14. **Quasistatic Process**: A very slow process that is fundamentally ***irreversible*** but done in such a way that the system coordinates are well defined at all times. Friction may be present as well as very small concentration gradients and small temperature differences through the system. Real processes are often modeled as quasistatic processes because in real processes things actually happen over time.
15. **Equlibrium Process**: State in which none of the system coordinates (extensive or intensive) vary with time – this is not the same as steady state! In fact, nothing happens so the word 'process' is somewhat meaningless.
16. **Thermodynamic Process**: A thermodynamic process occurs when the system goes from some initial equilibrium state S_1 to a new equilibrium state S_2. The system coordinates, eg., T, P etc. will change as a result of the process. The 'path' for the process is defined by a specification of the equation of state.
17. **Isothermal Process**: One carried out a constant temperature – generally the system wall would be diathermal so that heat transfer could occur but in the case of an adiabatic wall, electrical work could be done to add but not remove energy and so we have an example of a Carathe'odory inaccessible state.
18. **Adiabatic Process**: One without heat transfer between the system and surroundings, i.e., dQ = 0 over the course of the process.
19. **Reversible Process**: An infinitely slow process that can be reversed at any time in such a way as to restore BOTH the system and surrounding to their previous states. For a process to be reversible there must be no friction or finite temperature, pressure or concentration differences anywhere in the system. A reversible process is an equilibrium process in which nothing ever happens, and the use of reversibility as a model for a real process is often wildly optimistic.
20. **Equation of State**: An equation of the form $F(x_1, x_2, ...) = 0$ where $x_1, x_2....$ are the system variables or coordinates whose specification define the equilibrium state of the system, e.g., PV-RT=0 defines the variables that specify the equilibrium state of an ideal gas.

DW McClure, Emeritus Professor of Chemistry/Physics
Portland State University
2/15/2010