The term ‘boundary’ is encountered in several contexts in thermodynamics. Indeed the definition becomes more complicated as we concentrate on the thermodynamic properties of systems.

As a starting point, a boundary separates system and surroundings. A boundary is an infinitely thin surface separating system and surroundings such that the properties of system and surroundings change abruptly at the boundary. [1,2] In these terms a reaction vessel is part of the surroundings. We support this careful distinction by observing that if chemical reaction inside the system is exothermic, the liberated heat warms the reaction vessel. In this case, the boundary encloses the system. No molecules can either enter or leave the system. However heat is allowed to cross the boundary. Thus the whole universe is divided into system and surroundings [3], the only role of the boundary is to facilitate communication between system and surroundings. In these terms chemical substances, heat, and electric charge may cross a boundary between a system and surroundings.

In some cases the container (e.g. reaction vessel) may be considered part of the system. In many cases [4,5] it is correct to do so and so the boundary is again a hypothetical surface separating ‘reaction solution + reaction vessel’ and the surroundings.

In general terms, it is important to define the boundary for a given system. Another term for boundary is ‘envelope’ which indicates something which can be quite dynamic in terms of shape and volume rather than, for example, a glass vessel. Moreover the boundary may be selectively permeable to one or more chemical substances rather like the envelope of unit cells in living systems [6].

The term ‘boundary’ in the context of surface chemistry means a boundary phase (or, capillary phase) [7]. In such a phase there is a concentration gradient of one or more chemical substances across the boundary phase between system and surroundings. Indeed surface chemistry can be described as the chemistry of boundaries.
In summary we repeat the point that in a thermodynamic analysis of experimental results, a first requirement is that the system, boundary and surroundings are carefully defined. For the most part we assume that the boundary is an infinitely thin envelope separating system and surroundings.

Footnotes