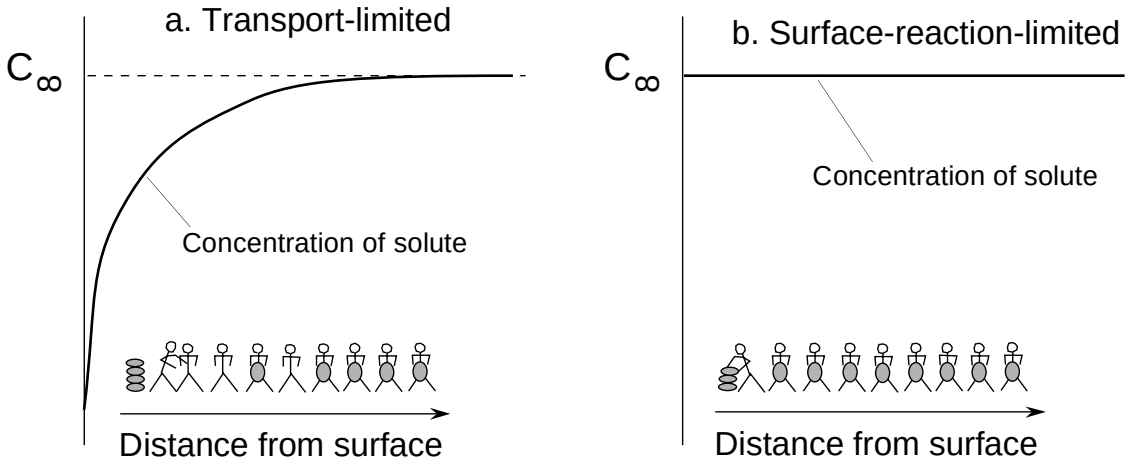
An explanation of transport-limited and surface-reaction-limited crystal growth

During floods, people are often observed building walls of sandbags to stop the water. Various logistical constraints often require that the bags of sand be moved by hand, and lines of people are formed to pass the bags along from one person to the next, until the bags reach the person building the wall of sandbags.

If the person building the wall works quickly, the people passing bags can't move bags quickly enough to keep him or her occupied. This is transport control or transport-limited growth: the transport process delays construction of the wall, and so transport is the rate-limiting step. In his or her desire to build the wall quickly, the builder may not only take bags from the nth person but may also move up the line to the (*n*-1)th person or even the (*n*-2)th person, grabbing their bags and putting them on the wall. The concentration of bags near the wall is thus lessened (Case a below).

If the person building the wall works slowly, each of the *n* persons in the line will be holding a bag, waiting to pass their bag along once the *n*th person has given his or her bag to the builder. This is surface-reaction control: the rate-limiting step is the placement of bags on the wall, and the concentration of bags is uniform along the line (Case b below).

In both cases, the people passing the bags are a one-dimensional analogy for diffusive transport, which is nature's tendency to produce random and thus effectively uniform distributions of ions or atoms within any one phase. A shorthand would be to say that they represent entropy.



C_∞ is concentration of solute in the bulk solution, and thus at an effectively infinite distance from the surface of the growing crystal.

The sandbag analogy is also useful in considering Ostwald's Law, which we will discuss later. If the line of people passing the sandbags works quickly, the person laying the bags is likely to hastily build a sloppy wall in which the bags are not carefully positioned. If the supply of bags is slow, the builder has time to carefully position each bag, making a much better-fitting wall.

The first condition is analogous to precipitation of a less stable polymorph from a solution highly supersaturated with respect to multiple polymorphs of a mineral. The second condition is analogous to precipitation of the most stable polymorph from a solution only slightly supersaturated with respect to the most stable polymorph. That's one way of looking at Ostwald's Law.