



EQUILIBRIUM

Equilibrium is a word denoting a static condition, the absence of change. In thermodynamics, it means not only the absence of change but the absence of any tendency toward change. Thus a system at equilibrium exists under conditions such that no change in state can occur. Since any tendency toward change is caused by a driving force of one kind or another, the absence of such a tendency indicates also the absence of any driving force. Different kinds of driving forces tend to bring about different kinds of change.

- imbalance of mechanical forces such as pressure on a piston tend to cause energy transfer as work
- temperature differences tend to cause the flow of heat gradients in chemical
- potential tend to cause substances to be transferred from one phase to another

THE PHASE RULE

The state of a pure homogeneous fluid is fixed whenever two intensive thermodynamic properties are set at definite values. In contrast, when two phases are in equilibrium, the state of the system is fixed when only a single property is specified. For example, a mixture of steam and liquid water in equilibrium at 101.325 kPa can exist only at 373.15 K (100°C). It is impossible to change the temperature without also changing the pressure if vapor and liquid are to continue to exist in equilibrium. For any system at equilibrium, the number of independent variables that must be arbitrarily fixed to establish its intensive state is given by the celebrated phase rule

$$F = 2 - \pi + N$$

Where N is number of chemical species

F called degree of freedom

π number of phases

The minimum number of degrees of freedom for any system is zero. When $F = 0$, the system is invariant; When $N = 1$, this number is 3, characteristic of a triple point. For example, the triple point of water, where liquid, vapor, and the common form of ice exist together in equilibrium, occurs at 273.16 K (0.01°C) and 0.0061 bar. Any change from these conditions causes at least one phase to disappear.

Ex :how many degree of freedom for the following

- a) liquid water in equilibrium with its vapor
- b) liquid water in equilibrium with a mixture of water vapor and nitrogen



c) a liquid solution of alcohol in water in equilibrium with its vapor

a) $F = 2 - \pi + N = 2 - 2 + 1 = 1$

That mean temperature or pressure but not both may be specified for system consisting of water in equilibrium with its vapor.

b) $F = 2 - 2 + 2 = 2$

now temperature and pressure may be independently varied , but they are fixed the system described can exist in equilibrium only at particular composition of vapor phase.

c) $F = 2 - 2 + 2 = 2$

THE REVERSIBLE PROCESS

A process is reversible when its direction can be reversed at any point by an infinitesimal change in external conditions.

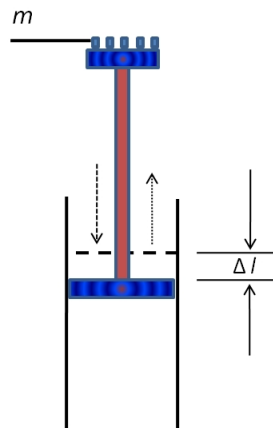
Reversible Expansion of a Gas

The apparatus shown in the below figure is imagined to exist in an evacuated space. The gas trapped inside the cylinder is chosen as the system; all else is the Surroundings . Expansion processes result when mass is removed from the piston.

Assumption

- friction less between piston and cylinder
- piston and cylinder neither absorb nor transmit heat
- ignore effects of gravity because mass of gas is small (low density)

This means that gravity-induced pressure gradients in the gas are very small relative to its pressure and that changes in potential energy of the gas are negligible in comparison with the potential-energy changes of the piston assembly.

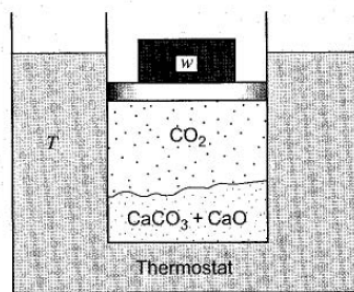




The piston confines the gas at a pressure just sufficient to balance the weight of the piston and all that it supports . there no tend for the system to change under equilibrium condition ., if the mass is suddenly slide from piston , the assembly accelerate upward ,reaching its maximum velocity at new balance point .

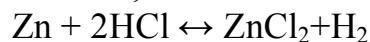
Reversible Chemical Reaction

The concept of a reversible chemical reaction is illustrated by the decomposition of calcium carbonate, which when heated forms calcium oxide and carbon dioxide gas. At equilibrium, this system exerts a definite decomposition pressure of CO₂ for a given temperature. When the pressure falls below this value, CaCO₃ decomposes. Assume that a cylinder is fitted with a frictionless piston and contains CaCO₃, CaO, and CO₂ in equilibrium. It is immersed in a constant-temperature bath, as shown in below figure , with the temperature adjusted to a value such that the decomposition pressure is just sufficient to balance the weight on the piston



If the weight is differentially increased, the CO₂ pressure rises differentially, and CO₂ combines with CaO to form CaCO₃, allowing the weight to fall slowly . The heat given off by this reaction raises the temperature in the cylinder, and heat flows to the bath. Decreasing the weight differentially sets off the opposite chain of events.

Chemical reactions can sometimes be carried out in an electrolytic cell, and in this case they may be held in balance by an applied potential difference. If such a cell consists of two electrodes, one of zinc and the other of platinum, immersed in an aqueous solution of hydrochloric acid, the reaction that occurs is:



The work of compression or expansion of a gas caused by the differential displacement of a piston in a cylinder is

$$dW = -pdV$$



The work done on the system is given by this equation only reversible process. The second requirement is that the system be no more than infinitesimally displaced from mechanical equilibrium with its surroundings. Processes for which these requirements are met are said to be mechanically reversible, and equation may be integrated

$$dW = - \int_{V_1}^{V_2} p dV$$