CHEMICAL ENGINEERING THERMODYNAMICS II (0905323)
01. SIMPLE EQUILIBRIA

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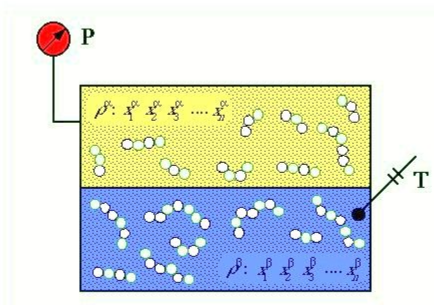
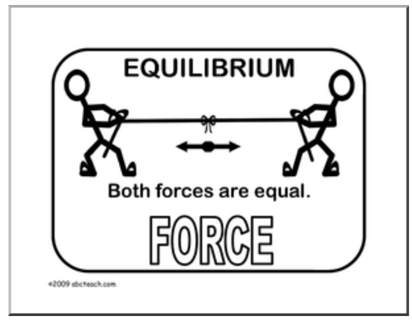
Outline

- Equilibrium
- Equilibrium is Dynamic
- Spontaneous Changes
- Types of Equilibrium
- Gibbs energy
- Phases and Phase Equilibria
- Phase Diagrams

Equilibrium

- A system is said to be at equilibrium if there is no change with time in any of the measurable properties of the system.





Equilibrium is Dynamic

- The fact that there is no measurable change does not mean that the system is static.
  - If two phases are at equilibrium, there is a steady interchange of molecules between the two phases. However, at equilibrium the flow of atoms or molecules in one direction is exactly equal to the flow in the other direction.
  - In all chemical reactions at equilibrium the concentrations of the reactants and products are not changing with time. That does not mean that the reaction has stopped. It means that the forward and reverse reactions are occurring at exactly the same rate, so that the net reaction rate (algebraic sum of the forward and backward reaction rates) is zero.

Spontaneous Changes

- Left to themselves, all systems in the world move toward a state of phase and chemical equilibrium.
- How fast natural systems move in the direction of phase and chemical equilibrium depends on mass transfer rates (phase equilibrium) and chemical reaction rates (chemical equilibrium).
- Knowing the equilibrium state tells us
  - In which direction the system will go.
  - How far the system is from its equilibrium state.
  - But not how fast it will move in that direction.

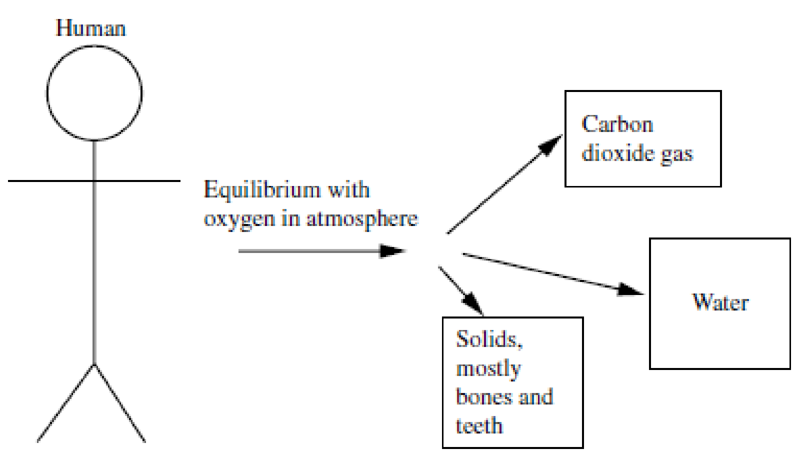
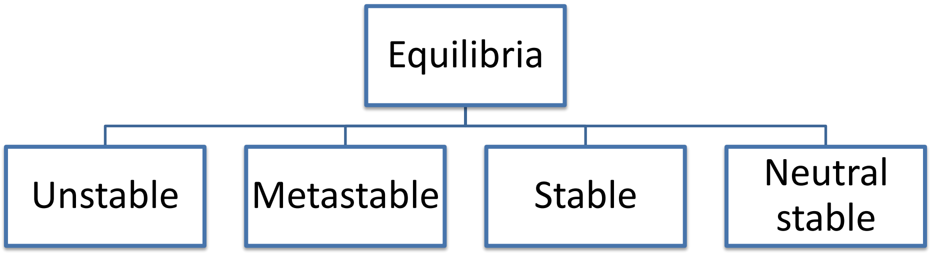
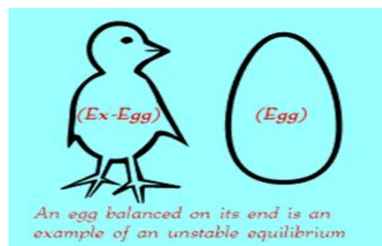


FIGURE 1.4 Equilibrium is not always desirable. If we bring a human to equilibrium with the oxygen in the atmosphere we will produce mostly water, carbon dioxide, and a solid residue made mostly of bones and teeth. We work hard at preventing this equilibrium, mostly by using the energy of the sun, concentrated in our foods.

Types of Equilibria





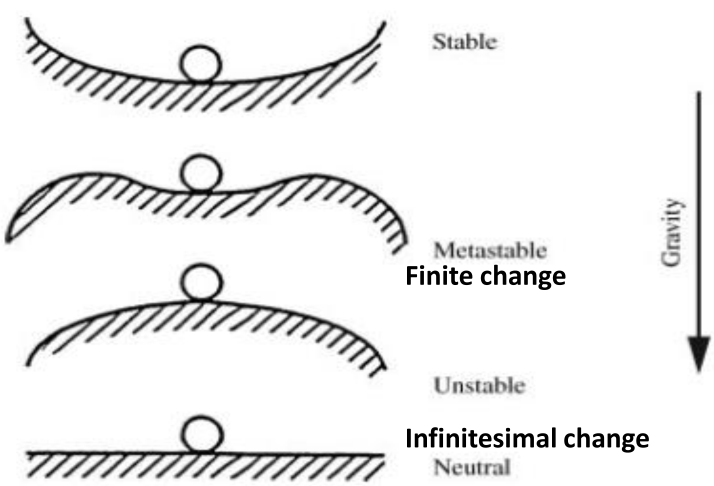
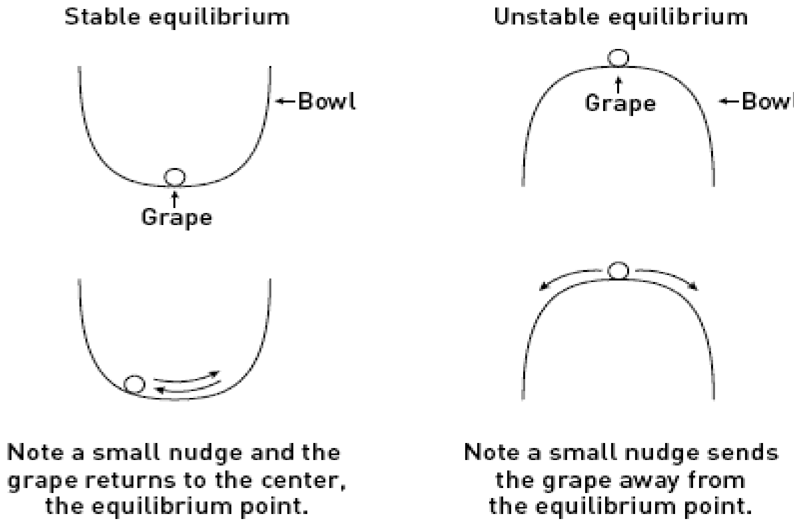


FIGURE 1.5 Mechanical models of stable, metastable, unstable, and neutral equilibrium.



Infinitesimal change

Gibbs Energy

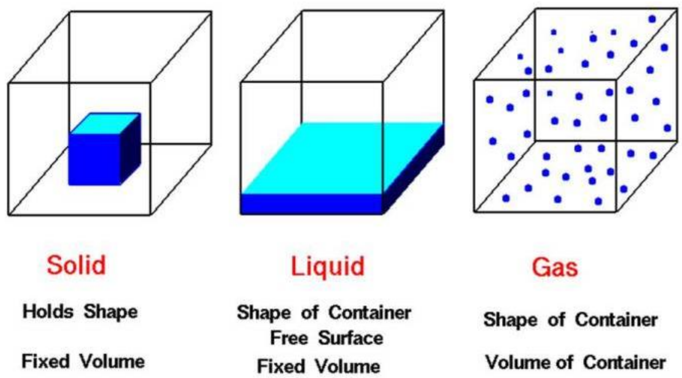
- On the basis of rigorous thermodynamics, all natural systems try to lower their Gibbs energy:

$$\begin{aligned} \text{Gibbs energy} &= H - TS \\ \text{Gibbs energy per mol or per unit mass} &= h - Ts \end{aligned} \qquad (1.1)$$

> For any differential equilibrium change, chemical or physical or both, at constant T and P,
>
> $$dG_{sys} = 0 \qquad (4.8)$$

Phases and Phase Equilibria

- A phase is a mass of matter, not necessarily continuous, in which there are no sharp discontinuities of any physical properties over short distances.
- An equilibrium phase is one that (in the absence of significant gravitational, electrostatic, or magnetic effects) has a completely uniform composition throughout.



Gas, Liquid and Solid Phases

- All gases form one phase. All gases are miscible, so that there can be only one gas phase present in any equilibrium system at any time.

Liquid Phase

- Liquids can form multiple phases.
- Hildebrand et al. [7] show an example of 10 liquid phases in equilibrium: hexane, analine, aqueous methyl cellulose, aqueous polyvinyl alcohol, aqueous mucilage, silicone oil, phosphorus, fluorocarbon, gallium, and mercury. That is probably the record.

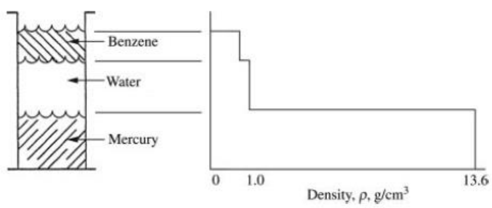
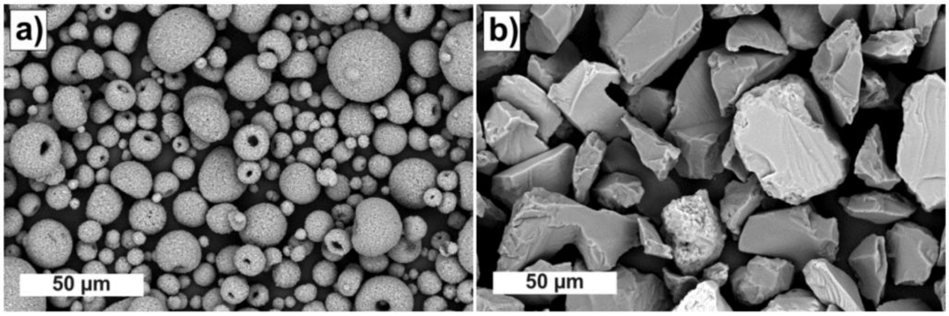


FIGURE 1.6 Appearance and elevation–density plot for three liquid phases at equilibrium.

https://www.youtube.com/watch?v=4EMUsPJtCoc
12 liquid layers

Solid Phase

- Homogeneous solids are single phases, for example diamond, pure metals, pure mineral crystals.
- Some apparently simple solids are not single phases, such as cast iron, steel, wood, bacon, grass.
- Large numbers of pure solid phases can be in thermodynamic equilibrium with each other; they generally do not mix significantly.
  - Many metals are solid solutions, such as brass, which is a solution of copper and zinc, and bronze, which is a solution of copper and tin.
  - These are formed by melting the metals together, in which state they dissolve each other, and then cooling.
  - Most steels are mostly iron, with some dissolved carbon, and small amounts of other metals.



Agglomerated and sintered Al_2O_3-13TiO_2 powder (Neoxid A103,HVOF cut) and (b) fused and crushed Al_2O_3-13TiO_2 powder (Amdry 6228,APS cut). SEM images.

Phase Diagrams

- A representation on some set of thermodynamic coordinates (many combinations of such variables are used in phase diagrams) showing which phase we would expect to find at a given set of values of the coordinates.
- The simplest phase diagram is a vapor-pressure curve. Figure 1.8 shows the vapor-pressure curve for water.

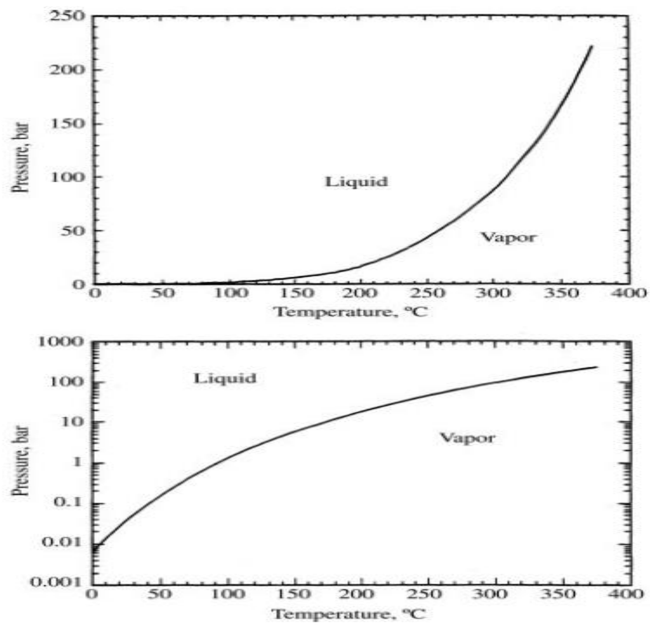


FIGURE 1.8 Vapor liquid equilibrium curve for water–steam, in arithmetic and logarithmic coordinates [6]. The range of values shown is so large that on arithmetic coordinates the low-temperature values disappear into the horizontal axis. On a logarithmic scale they are all visible.

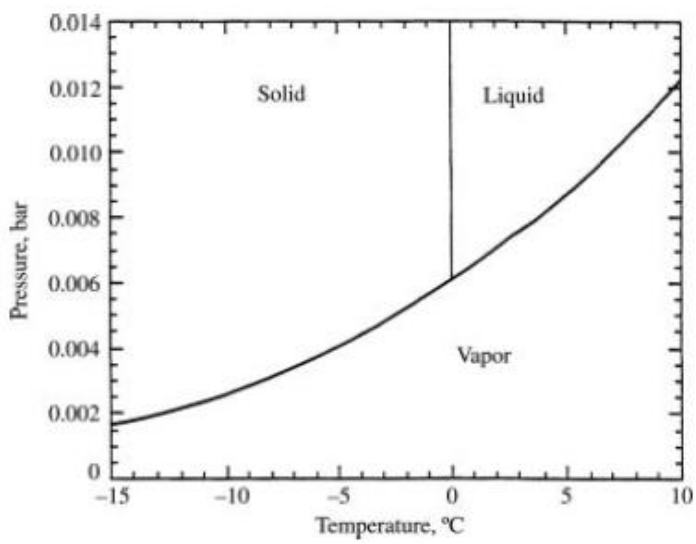
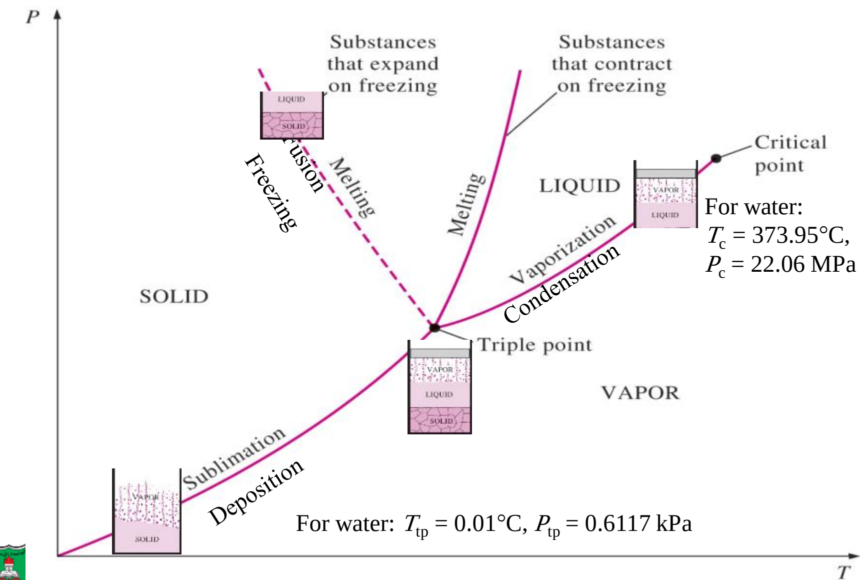


FIGURE 1.9 Extension of Figure 1.8 (arithmetic part only) to temperatures below the normal freezing point of water, showing the formation of ice [5, 6]. This is all at low pressures; the maximum pressure shown is 0.014 bar. The rightmost curve is the same as part of the curve in Figure 1.8, simply drawn on a much expanded pressure scale.

P-T Projection



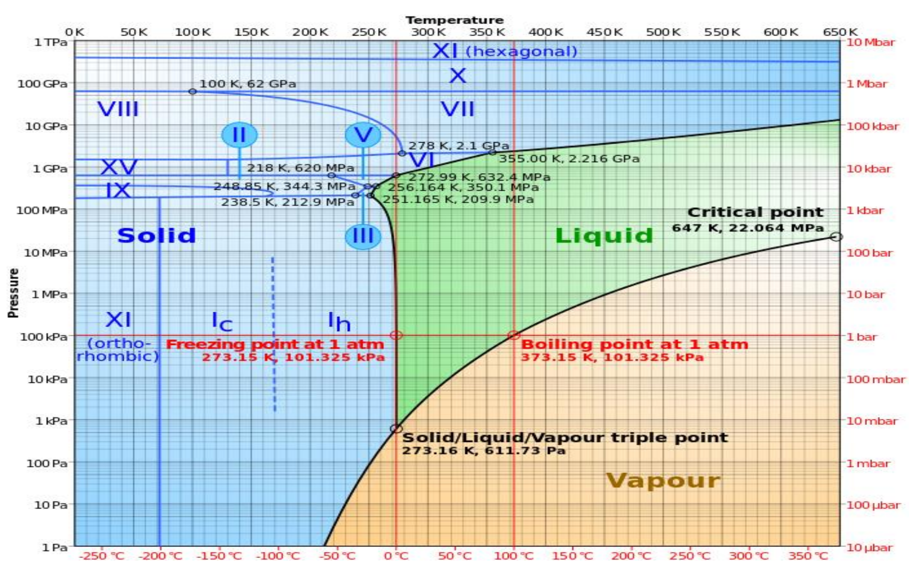
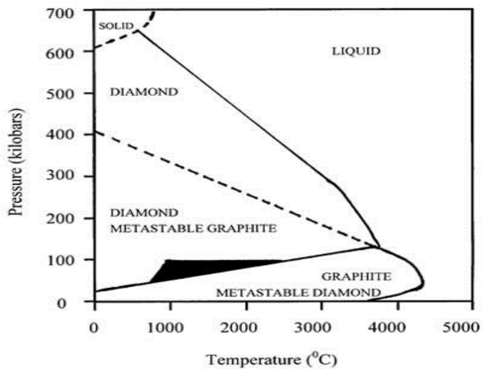
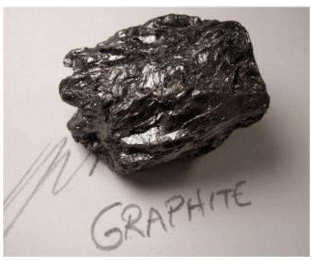
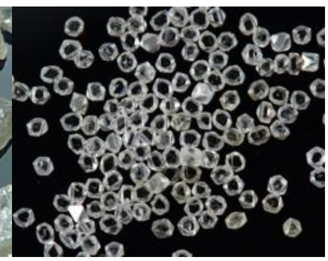


FIGURE 1.10 Phase diagram for water at high pressures, showing the five solid forms that do not exist at normal pressures. The pressures shown are so high that the normal vapor–liquid equilibrium curve (Figure 1.8) disappears into the horizontal axis.

Carbon phase diagram



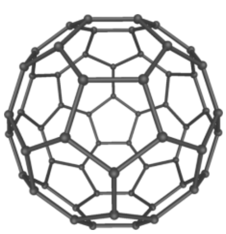


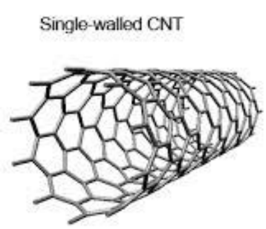


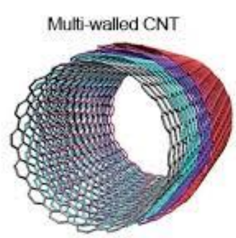
Graphite

Natural diamond

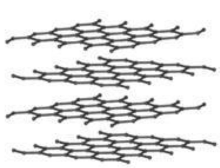
Industrial diamond

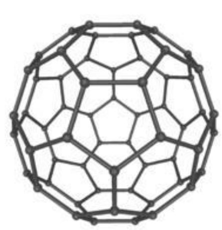


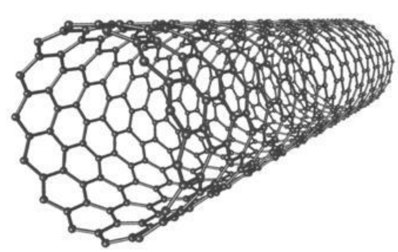




Bucky balls







Graphene

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23