

J 10/21

$$\begin{aligned}
 K_T (C_p - C_v) &= VT \alpha_r^2 & \Rightarrow & \boxed{C_p \geq C_v \geq 0} \\
 \frac{C_p}{C_v} &= \frac{K_T}{K_S} & \Rightarrow & \boxed{K_S \geq 0} \\
 C_p (K_T - K_S) &= TV \alpha_r^2 & \Rightarrow & \boxed{K_T \geq K_S}
 \end{aligned}$$

Le Chatelier's principle:

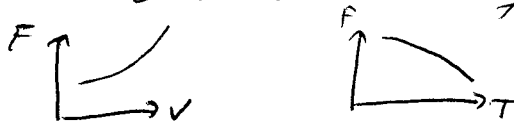
If a system is in stable equilibrium, then any spontaneous change in its parameters must bring about processes which tend to restore the system to equilibrium.

Consequences for free energies:

$$\left(\frac{\partial^2 F}{\partial T^2} \right)_{V, \{N_i\}} = - \left(\frac{\partial S}{\partial T} \right)_{V, \{N_i\}} = - \frac{C_{V, \{N_i\}}}{T} \leq 0$$

$$\left(\frac{\partial^2 F}{\partial V^2} \right)_{T, \{N_i\}} = - \left(\frac{\partial P}{\partial V} \right)_{T, \{N_i\}} = \frac{1}{V K_{T, \{N_i\}}} \geq 0$$

\Rightarrow The Helmholtz free energy is a concave function of temperature and a convex function of volume



$$\left(\frac{\partial^2 G}{\partial T^2} \right)_{P, \{N_i\}} = - \left(\frac{\partial S}{\partial T} \right)_{P, \{N_i\}} = - \frac{C_{P, \{N_i\}}}{T} \leq 0$$

$$\left(\frac{\partial^2 G}{\partial P^2} \right)_{T, \{N_i\}} = \left(\frac{\partial V}{\partial P} \right)_{T, \{N_i\}} = -V K_{T, \{N_i\}} \leq 0$$

\Rightarrow The Gibbs free energy is a concave function of temperature and a concave function of pressure.

$$\left(\frac{\partial^2 H}{\partial P^2}\right)_{S, \{N_i\}} = \left(\frac{\partial V}{\partial P}\right)_{S, \{N_i\}} = -V\kappa_{S, \{N_i\}} \leq 0$$

$$\left(\frac{\partial^2 H}{\partial S^2}\right)_{P, \{N_i\}} = \left(\frac{\partial T}{\partial S}\right)_{P, \{N_i\}} = \frac{T}{C_{P, \{N_i\}}} \geq 0$$

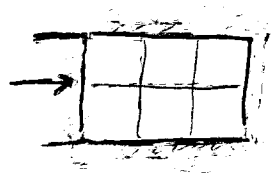
⇒ The enthalpy is a concave function of pressure and a convex function of entropy.

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_{S, \{N_i\}} = -\left(\frac{\partial P}{\partial V}\right)_{S, \{N_i\}} = \frac{1}{V\kappa_{S, \{N_i\}}} \geq 0$$

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V, \{N_i\}} = \left(\frac{\partial T}{\partial S}\right)_{V, \{N_i\}} = \frac{T}{C_{V, \{N_i\}}} \geq 0$$

⇒ The internal energy is a convex function of volume and a convex function of entropy.

I.7 Mixing of ideal gases



m compartments with one ^{ideal} gas each
 walls can move and transfer heat
 ⇒ *P, T* constant all over the system

Gibbs free energy: sum of individual Gibbs free energies

$$G_I(P, T, n_1, \dots, n_m) = -\sum_{j=1}^m n_j RT \ln \left[\frac{T^{5/2}}{P} \right] + G_I^{(0)}$$

↑
some constant

Take walls away \Rightarrow mixture of ideal gases

Equation of state:

$$P = \sum_{j=1}^m P_j$$

with $P_j = \frac{n_j RT}{V}$ "partial pressure"

Useful quantities to describe mixtures:

$$\text{mole fraction } x_j = \frac{n_j}{\sum_{i=1}^m n_i} \in [0, 1]$$

Gibbs free energy of mixture:

$$\begin{aligned} G_F(P, T, n_1, \dots, n_m) &= - \sum_{j=1}^m n_j RT \ln \left[\frac{T^{5/2}}{P_j} \right] + \overset{\text{same constant}}{\downarrow} G_F^{(0)} \\ &= - \sum_{j=1}^m n_j RT \ln \left[\frac{T^{5/2}}{x_j P} \right] + G_F^{(0)} \\ &= G_I(P, T, n_1, \dots, n_m) + \sum_{j=1}^m n_j RT \ln x_j + G_F^{(0)} - G_I^{(0)} \end{aligned}$$

$$\Rightarrow \Delta G = G_F - G_I = \sum_{j=1}^m n_j RT \ln x_j + G_F^{(0)} - G_I^{(0)}$$

corresponding change in entropy:

$$\Delta S_{\text{mix}} = - \sum_{j=1}^m n_j R \ln(x_j) \geq 0 \quad \text{"mixing entropy"}$$

The entropy increase even occurs if there was the same gas in all compartments $\circ \rightarrow$ Gibbs paradox

\rightarrow resolved by quantum mechanics

I.8 Summary

concepts: state variables
 reversible and irreversible processes
 Carnot process
 entropy
 thermodynamic potentials
 response functions

facts: zeroth to third law
 extremization principles
 degrees of freedom of a system
 local equilibrium conditions
 local stability conditions

tools: exact differentials
 relations between partial derivatives
 equations of state
 Maxwell relations

1/10/21