

Equations

Henrik Modahl Breitenstein
(Dated: October 6, 2021)

FIRST LAW

Energy is always conserved. It can not be made or disappear for a closed system.

$$\Delta U = Q + W . \quad (1)$$

Where U is the internal energy, Q is the heat and W is the work.

SECOND LAW

For a isolated system the change in entropy is never below zero.

$$\Delta S \geq 0 \quad (2)$$

For reference

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T} dT \quad (3)$$

THIRD LAW

If the entropy is constant, then the temperature doesn't change.

$$\begin{aligned} \frac{\partial S_1}{\partial U_1} &= \frac{\partial S_2}{\partial U_2} \leftrightarrow T_1 = T_2 , \text{ Thermodynamic} \\ \frac{\partial S_1}{\partial V_1} &= \frac{\partial S_2}{\partial V_2} \leftrightarrow P_1 = P_2 , \text{ Mechanical} \\ \frac{\partial S_1}{\partial N_1} &= \frac{\partial S_2}{\partial N_2} \leftrightarrow \mu_1 = \mu_2 , \text{ Chemical} \end{aligned}$$

MULTIPLICITY

$$S = k \ln \Omega \quad (4)$$

$$S_{\text{total}} = S_A + S_B$$

Stirling's approximation

$$N! \approx N^N e^{-N} \sqrt{2\pi N}$$

For monatomic ideal gas

$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{(\frac{3N}{2} - 1)!} \left(\sqrt{2mU} \right)^{3N-1}$$

Sackur-Tetrode equation

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

For mixing

$$\Delta S_{\text{mixing}} = -R[x \ln x + (1-x) \ln(1-x)]$$

$$G_{\text{mixing}} = G - T\Delta S_{\text{mixing}}$$

Stays in mixed state since

$$G_{\text{mixing}} < G$$

STATE VARIABLES AND FUNCTIONS

When we specify the equilibrium with a given value of some variable, that variable is a state variable.

$$N, V, P, T, \mu, U, S, H, F, G$$

A state variable is a variable dependent on other variables.

Extensive variables are variables scaling with the system.

$$N, V, U, S, m, C_V$$

Intensive variables are variables which stay constant through system-scaling.

$$T, P, \mu, \rho$$

ENERGIES

Thermodynamic Identity

$$dU = TS - PV + \mu N \quad (5)$$

Enthalpy

$$H \equiv U + PV = H(S, P, N) \quad (6)$$

Helmoltz

$$F \equiv U - TS = F(T, V, N) \quad (7)$$

Gibbs

$$G \equiv U - TS + PV = G(T, P, N) \quad (8)$$

Grand

$$\Phi \equiv U - TS - \mu N = \Phi(V, T, N) \quad (9)$$

Definitions

The different energy-definitions gives us new ways to redefine variables.

$$T = \left(\frac{\partial U}{\partial S} \right)_{N,V} = \left(\frac{\partial H}{\partial S} \right)_{N,P} \quad (10)$$

$$P = \left(\frac{\partial S}{\partial V} \right)_{N,U} = - \left(\frac{\partial F}{\partial V} \right)_{N,T} = - \left(\frac{\partial \Phi}{\partial V} \right)_{\mu,T} \quad (11)$$

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V} = \left(\frac{\partial H}{\partial N} \right)_{S,P} = \left(\frac{\partial F}{\partial N} \right)_{V,T} = \left(\frac{\partial G}{\partial N} \right)_{T,P} \quad (12)$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{N,V} \quad (13)$$

$$V = \left(\frac{\partial H}{\partial P} \right)_{N,S} = \left(\frac{\partial G}{\partial P} \right)_{N,T} \quad (14)$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_{N,V} = - \left(\frac{\partial G}{\partial T} \right)_{N,P} = - \left(\frac{\partial \Phi}{\partial T} \right)_{\mu,V} \quad (15)$$

$$N = \left(\frac{\partial \Phi}{\partial \mu} \right)_{V,T} \quad (16)$$

MAXWELLS RELATIONS

For a state function f with natural variables x and y , we have the symmetry:

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \quad (17)$$

With U , G , H , and F this gives us the relations

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$$

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

$$- \left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P$$

SECOND LAW FOR F AND G

Hold (N, V, T) constant

$$\Delta F \leq 0.$$

Hold (N, P, T) constant

$$\Delta G \leq 0.$$

TROUTON'S RULE

$$\Delta S_{\text{vap}} = \frac{\Delta H}{T_b} \approx 85 \frac{J}{\text{mol} \cdot K}$$

CLASUSIS-CLAPEYRON RELATION

$$\ln \frac{P_1}{P_2} = - \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

OSMOTIC PRESSURE

Van't Hoffs formula

$$(P_1 - P_2) = \frac{kT n_B}{V} = \frac{RT n_B}{V}$$

I. CONSTANTS

$$R = 8.3145 \frac{J}{mol \cdot K}$$

Gas constant

$$k = 1.38064852 \cdot 10^{-23} m^2 kg s^{-2} K^{-1}$$