Auxiliary Function

1 Overview

Now we have formally introduced a set of TD properties that are sufficient for the development of chemical thermodynamics, but it could be more convenient to use introduce some new TD properties with special physical interpretations.

Enthalpy:

$$H = U + pV, h = u + pv \tag{1}$$

Gibbs Free Energy (Gibbs Function, notice that this is different from **Gibbs Equation**):

$$G = H - TS, g = h - Ts \tag{2}$$

Helmholtz Free Energy:

$$F = U - TS, f = u - Ts \tag{3}$$

2 Enthalpy

Based on the definition of enthalpy:

$$H_2 - H_1 = U_2 - U_1 + p_2V_2 - p_1V_1 \tag{4}$$

Recall the first law for closed system:

$$U_2 - U_1 = Q_{12} + W_{12} \tag{5}$$

Therefore:

$$\Delta H_{12} = Q_{12} + W_{12} + p_2V_2 - p_1V_1 \tag{6}$$

2.1 Constant Pressure

$$W_{12} = -\int pdV = -p(V_2 - V_1) \tag{7}$$

So we have:

$$\Delta H_{12} = Q_{12} \tag{8}$$

2.2 Constant Volume

Because only pdV work, so $W_{12} = 0$, then:

$$\Delta H_{12} - p_2 V_2 + p_1 V_1 = Q_{12} \tag{9}$$

So we have:

$$\Delta U_{12} = Q_{12} \tag{10}$$

2.3 Isolated System

Based on definition of isolated system, we have:

$$\Delta U = 0, \Delta V = 0, Q = W = 0 \tag{11}$$

However, **enthalpy is not conserved!**

$$\Delta H_{12} = V(p_2 - p_1) \tag{12}$$

This is the classical process that there is chemical reaction in rigid adiabatic vessel.

3 Useful Work

Gibbs energy and Helmholtz energy actually represent the useful work for the reacting system. Recall the first and second law:

$$\Delta U_{12} = Q + W_{in} \tag{13}$$

$$\Delta S_{12} = Q/T + P_s \tag{14}$$

If we consider CM with changes from state 1 to state 2 **at constant T because of a reaction (change in composition.)** Therefore, we can get the work out (notice here the work includes pdV work):

$$W_{out} = -W_{in} = -\Delta U_{12} + T\Delta S_{12} - TP_s \tag{15}$$

We try to get maximum work out of reversible process.

3.1 Helmholtz Energy

If **constant volume, no pdV work**:

$$W_{u,max,out} = -[(U_2 - TS_2) - (U_1 - TS_1)] = -(F_2 - F_1) \tag{16}$$

So **Helmholtz energy is for constant temperature and volume.**

3.2 Gibbs Energy

If constant pressure:

$$W_{u,max,out} = -[(U_2 + pV_2 - TS_2) - (U_1 + pV_1 - TS_1)] = -(G_2 - G_1) \tag{17}$$

So **Gibbs energy is for constant temperature and pressure.**

4 Conditions for Chemical Equilibrium

Similarly, we consider CM with changes from state 1 to state 2 at constant T because of a reaction (change in composition.) **But this time, we assume no other work but pdV work.**

Also start with fist and second law:

$$dU = \delta Q + \delta W = \delta Q - pdV \tag{18}$$

$$dS = \delta Q/T + \delta P_s \tag{19}$$

Therefore, the entropy production could be expressed as:

$$\delta P_s = TdS - dU - pdV \geq 0 \tag{20}$$

4.1 Isolated System

Which means U, V are constant. Then:

$$TdS - \cancelto{0}{dU} - \cancelto{0}{pdV} \geq 0 \tag{21}$$

$$dS \geq 0 \tag{22}$$

Therefore, the chemical equilibrium condition of this case when the composition reach S_{max} composition.

4.2 Constant T, V

$$TdS - dU - \cancelto{0}{pdV} \geq 0 \tag{23}$$

Recall that:

$$dF = d(U - TS) = dU - TdS - \cancelto{0}{SdT} \tag{24}$$

So:

$$dF \leq 0 \tag{25}$$

Therefore, the chemical equilibrium condition of this case when the composition reach F_{min} composition.

4.3 Constant T, P

$$TdS - dU - pdV \geq 0 \tag{26}$$

$$\cancelto{0}{SdT} + TdS - dU - pdV - \cancelto{0}{Vdp} \geq 0 \tag{27}$$

$$d(ST) - dU - d(pV) = d(ST) - dH = -dG \geq 0 \tag{28}$$

Therefore, the chemical equilibrium condition of this case when the composition reach G_{min} composition.