

5.12 - Using the Fact that S is a State Function to Determine the Dependence of S on V and T

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

↳ Because $\frac{1}{T}$ and $\frac{P}{T}$ are greater than zero, the entropy of a system increases with the volume @ constant internal energy.

This can be rewritten to evaluate $(\partial S / \partial T)_V$ and $(\partial S / \partial V)_T$

↳ Because V isn't used experimentally we derive an equation for dS with the dependence of V and T.

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$dS = \frac{1}{T} [C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV] + \frac{P}{T} dV = \frac{C_V}{T} dT + \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

Equating these two coefficients of dT and dV can allow us to derive:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \text{ and } \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

The second derivative of this equation yields to

$$\left(\frac{\partial}{\partial V} \left(\frac{\partial S}{\partial T}\right)_V\right)_T = \frac{1}{T} \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T}\right)_V\right)_T$$

From this we can calculate entropy @ constant volume using

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial V}\right)_T\right)_V = \frac{1}{T} \left[\left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T\right)_V\right] - \frac{1}{T^2} \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \rightarrow dS = \frac{C_V}{T} dT, \text{ constant } V.$$

Substituting the expressions for the mixed second derivative into first equation

To make it a direct comparison with experiment, we can now incorporate the fact that dS is an exact differential.

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

↳ This equation is used to calculate the U of the system if the equation of state for the substance is known.

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

*** Those two equations allow for an equation to be obtained for the dependence of entropy on volume under constant temperature conditions

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

$$dS = \frac{C_V}{T} dT + \frac{\alpha}{\kappa} dV$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{\alpha}{\kappa} dV$$

This result applies to a single-phase system of a liquid, solid, or gas that undergoes a transformation from the initial result T_i, V_i to T_f, V_f .

5.13 - The Dependence of S on T and P

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$U = H - PV \rightarrow$ From this we can write the total differential dU as

$$dU = TdS - PdV = dH - \underbrace{PdV - VdP}_{\text{Can be rearranged to } 0}$$

$$dS = \frac{1}{T} dH - \frac{V}{T} dP$$

This can be written in terms of P and not V.

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$= C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

Substitute dH into equation

$$dS = \frac{C_P}{T} dT + \frac{1}{T} \left[\left(\frac{\partial H}{\partial P}\right)_T - V \right] dP = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Because dT and dP must be the same on both sides of the equation so

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} + \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T} \left[\left(\frac{\partial H}{\partial P}\right)_T - V \right]$$

Will always remain positive so we can

conclude that S is a monotonically increasing function of the temperature.

In order to determine experimentally we equate the mixed second partial derivatives of $\left(\frac{\partial S}{\partial T}\right)_P$ and $\left(\frac{\partial S}{\partial P}\right)_T$

Mixed partial derivatives can be evaluated by

$$\left(\frac{\partial}{\partial P} \left(\frac{\partial S}{\partial T}\right)_P\right)_T = \frac{1}{T} \left(\frac{\partial C_P}{\partial P}\right)_T = \frac{1}{T} \left(\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial T}\right)_P\right)_T$$

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

Equating the two

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial P}\right)_T\right)_P = \frac{1}{T} \left[\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial P}\right)_T - \left(\frac{\partial V}{\partial T}\right)_P \right] - \frac{1}{T^2} \left[\left(\frac{\partial H}{\partial P}\right)_T - V \right]$$

$$\frac{1}{T} \left(\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial P}\right)_T\right)_P = \frac{1}{T} \left[\left(\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial P}\right)_T\right)_P - \left(\frac{\partial V}{\partial T}\right)_P \right] - \frac{1}{T^2} \left[\left(\frac{\partial H}{\partial P}\right)_T - V \right]$$

$$\rightarrow \text{Simplifies to: } \left(\frac{\partial H}{\partial P}\right)_T - V = -T \left(\frac{\partial V}{\partial T}\right)_P$$

Using this the pressure dependence of the entropy at constant temperature can be written as

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

$$dS = \frac{C_P}{T} dT - V\beta dP$$

By \int



$$\Delta S = \int_{T_i}^{T_f} \frac{C_P}{T} dT - \int_{P_i}^{P_f} V\beta dP$$

This result applies to a single-phase system of a pure liquid, solid, or gas that undergoes a transformation from the initial result T_i, P_i to T_f, P_f .

6.1 - The Gibbs Energy and the Helmholtz Energy

Clausius Inequality - The Fundamental expression governing spontaneity

Can be written as $Tds \geq dq$

The equality is satisfied only for a reversible process.

$$dq = dU - dw$$

This can now be used to rewrite the eq above as

$$Tds \geq dU - dw \text{ or, equivalently, } -dU + dw + Tds \geq 0$$

This equation expresses the condition of spontaneity for an arbitrary process in terms of the changes in the state functions U, V, S, T as well as the path-dependent functions $P_{ext}dV$ and $dw_{nonexpansion}$.

$$-dU - P_{ext}dV + dw + Tds \geq 0$$

In order to distinguish from expansion work and nonexpansion work, this equation can be rewritten

Assuming that this is for an isolated process $w=0$, and $dU=0$, this can be written

$$ds \geq 0$$

Assuming that this is for an isothermal process, $Tds = d(TS)$

$$-dU + Tds \geq -dw_{expansion} - dw_{nonexpansion}$$

$$d(U - TS) \leq dw_{expansion} + dw_{nonexpansion}$$

Helmholtz Energy - The combination of state functions $U - TS$, which has the units of energy, defines a new state function abbreviated A .

Using the definition, the general condition of spontaneity for isothermal process becomes

$$dA - dw_{expansion} - dw_{nonexpansion} \leq 0$$

This can be used to calculate the maximum work that a system can do on the surroundings in an isothermal process

$$dw_{total} = dw_{expansion} + dw_{nonexpansion} \geq dA$$

For chemical reactions, conditions are studied under constant pressure.

Using an isothermal constant pressure process. At constant P and T ,

$$PdV = d(PV) \text{ and } Tds = d(TS). \text{ Equation can be written}$$

$$d(U + PV - TS) = d(H - TS) \leq dw_{nonexpansion}$$

Gibbs Energy - The combination of state functions $H - TS$, which has the units of energy, abbreviated G .

The condition for spontaneity and equilibrium for an isothermal process at constant pressure becomes

$$dG - dw_{nonexpansion} \leq 0$$

6.1 - Continued.

- For a reversible process, the equality holds, and the change in the Gibbs energy is a measure of the maximum nonexpansion work that can be produced in the transformation.

$dG \leq 0 \rightarrow$ When pressure and temperature are held constant

$$dS - \frac{\delta q}{T} \geq 0 \quad \rightarrow \text{Recall } dS_{\text{surroundings}} = -\delta q/T$$

$$dS + dS_{\text{sur}} \geq 0$$

- By introducing G and A , it is no longer necessary to consider the surroundings explicitly.

Maximum nonexpansion work

\rightarrow Used to calculate the electrical work produced by a reaction in an electrochemical cell.

$$\Delta G_R = \Delta H_R - T\Delta S_R$$

$\rightarrow R \rightarrow$ Process of interest is chemical reaction.

Depends on the [reactants] and [products] until $\Delta G_R = 0$
 \rightarrow Equilibrium

$$\Delta A_R$$

*** In order for ΔG_R to determine an isothermal chemical transformation is spontaneous there are two contributions: ΔH_R and $T\Delta S_R$.

$$\Delta U_R$$

$$T\Delta S_R$$

- The entropic contributions to ΔG_R is greater for higher temperatures.
- A chemical transformation is always spontaneous if $\Delta H_R < 0$ and $\Delta S_R > 0$ (exothermic).
- A chemical transformation is never spontaneous if $\Delta H_R > 0$ and $\Delta S_R < 0$ (endothermic).
- For all other cases, the relative magnitudes of ΔH_R and $T\Delta S_R$ determine if the chemical transformation is spontaneous.
- If the chemical reaction is not spontaneous, then the reverse process is spontaneous.
- If $\Delta G_R = 0$, the reaction mixture is at equilibrium, and neither direction of change is spontaneous.

$$\Delta A_R = \Delta U_R - T\Delta S_R \quad \text{For constant } V \text{ and } T.$$

6.2 - The Differential Forms of U , H , A , and G

U and $H \rightarrow$ Used to calculate changes in Energy for processes.

A and $G \rightarrow$ Used to calculate the direction in which processes evolve and the maximum work the reactions can produce.

$$\begin{aligned} \rightarrow dU &= Tds - PdV \\ H = U + PV &\rightarrow dH = Tds - PdV + PdV + VdP = Tds + VdP \\ A = U - TS &\rightarrow dA = Tds - PdV - Tds - SdT = -SdT - PdV \\ G = H - TS = U + PV - TS &\rightarrow dG = Tds + VdP - Tds - SdT = -SdT + VdP \end{aligned}$$

*These differential forms express:

- Internal Energy $\rightarrow U(S, V)$
- Enthalpy $\rightarrow H(S, P)$
- Helmholtz Energy $\rightarrow A(T, V)$
- Gibbs Energy $\rightarrow G(T, P)$

Natural Variables - Used because the differential expressions are compact.

Because U, H, A , and G are state functions, two different equivalent expressions such as those written for $dU \rightarrow dU = Tds - PdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$

For this to be true \rightarrow

$$\begin{aligned} \left(\frac{\partial U}{\partial S}\right)_V &= T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \\ \left(\frac{\partial H}{\partial S}\right)_P &= T \quad \text{and} \quad \left(\frac{\partial H}{\partial P}\right)_S = V \\ \left(\frac{\partial A}{\partial T}\right)_V &= -S \quad \text{and} \quad \left(\frac{\partial A}{\partial V}\right)_T = P \\ \left(\frac{\partial G}{\partial T}\right)_P &= -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_T = V \end{aligned}$$

Maxwell Relations:

$$\begin{aligned} \rightarrow \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{K} \\ -\left(\frac{\partial S}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_P = V\beta \end{aligned}$$

*Because $ds = \frac{dq_{\text{reversible}}}{T}$, a transformation @ constant entropy refers to a reversible adiabatic process.

6.3 - The Dependence of the Gibbs and Helmholtz Energies on P, V, and T.

$\left(\frac{\partial A}{\partial T}\right)_V = -S$ and $\left(\frac{\partial A}{\partial V}\right)_T = -P$ - The Helmholtz energy of a pure substance decreases as either the temperature or the volume increases.

$\left(\frac{\partial G}{\partial T}\right)_P = -S$ and $\left(\frac{\partial G}{\partial P}\right)_T = V$ - The Gibbs energy decreases with increasing temperature, it increases with increasing pressure.

$$\int_{P^0}^P dG = G(T, P) - G^0(T, P^0) = \int_{P^0}^P V dP'$$

↳ where P^0 must be 1 bar.

Can be written in terms for solids

and liquids as

$$G(T, P) = G^0(T, P^0) + \int_{P^0}^P V dP' \approx G^0(T, P^0) + V(P - P^0)$$

Can be written in terms of a reversible path and assuming ideal gas behavior

$$G(T, P) = G^0(T) + \int_{P^0}^P V dP' = G^0(T) + \int_{P^0}^P \frac{nRT}{P'} dP' = G^0(T) + nRT \ln\left(\frac{P}{P^0}\right)$$

Using the chain rule:

$$\left(\frac{\partial [G/T]}{\partial T}\right)_P = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_P + G \frac{\partial [1/T]}{\partial T}$$

$$\text{Gibbs-Helmholtz eq} = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} = -\frac{S}{T} - \frac{G}{T^2} = -\frac{G+TS}{T^2} = -\frac{H}{T^2}$$

$$\rightarrow \left(\frac{\partial [G/T]}{\partial [1/T]}\right)_P = \left(\frac{\partial [G/T]}{\partial T}\right)_P \left(\frac{\partial T}{\partial [1/T]}\right) = -\frac{H}{T^2} (-T^2) = H$$

$$\int_{T_1}^{T_2} d\left(\frac{\Delta G}{T}\right) = \int_{T_1}^{T_2} \Delta H d\left(\frac{1}{T}\right)$$

$$\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H(T_1) \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$