

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

I. General eqn for the dependence of S on V and T (can be applied to solids, liquids, and real gases)

A.) dS is an exact differential

$$1.) \text{Equation: } dS = \frac{1}{T} dU + \frac{P}{T} dV$$

a.) since $\frac{1}{T}$ and $\frac{P}{T} > 0$, entropy of system inc. with the internal energy at constant volume

b.) entropy of a system inc. w/ volume at const. internal energy.

$$2.) \text{Total differential } dS: dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

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

$$\text{i.) Equating coefficients of } dT \text{ and } dV: \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \text{ and } \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} [P + \left(\frac{\partial U}{\partial V}\right)_T]$$

$$3.) \text{Temperature dependence of entropy: } dS = \frac{C_V}{T} dT, \text{ const. } V$$

$$\text{a.) relation: } \left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial V} \left(\frac{\partial S}{\partial T}\right)_V\right)_T$$

$$\text{i.) Mixed second derivatives: } \left(\frac{\partial}{\partial V} \left(\frac{\partial S}{\partial T}\right)_V\right)_T = \frac{1}{T} \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T}\right)_V\right)_T$$

$$\text{ii.) } \left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial V}\right)_T\right)_V = \frac{1}{T} \left[\left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T\right)_V \right] - \frac{1}{T^2} [P + \left(\frac{\partial U}{\partial V}\right)_T]$$

$$\text{A.) Simplified eqn: } P + \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V$$

i.) Eqn provides way to calculate the internal pressure of the system if the eqn of state for the substance is known.

$$4.) \text{dependence of entropy on volume under const. temp: } \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = - \frac{(2V/\partial T)_P}{(2V/\partial P)_T} = \frac{\beta}{K}$$

a.) β = coefficient for thermal expansion at const. Pressure

b.) K = isothermal compressibility coefficient

$$5.) \text{Eqn: } dS = \frac{C_V}{T} dT + \frac{\beta}{K} dV$$

$$\text{a.) Integrate for reversible path: } \Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{\beta}{K} dV$$

i.) applies to single-phase system of liq, solid or gas provided no phase change or chemical rxns occur.

5.13 The Dependence of S on T and P

I. How S varies with T and P

$$\text{A.) Total differential: } dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = \frac{1}{T} dH - \frac{V}{T} dP$$

$$\text{B.) Total differential } dU = TdS - PdV = dH - PdV - VdP$$

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

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

$$\text{a.) } \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\text{b.) } \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T} \left[\left(\frac{\partial H}{\partial P}\right)_T - V \right]$$

i.) $\frac{C_P}{T}$ is positive for all substances $\therefore S$ monotonically increasing function of temp.

$$\text{ii.) Equate mixed partial derivatives: } \left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial P}\right)_T\right)_P = \left(\frac{\partial}{\partial P} \left(\frac{\partial S}{\partial T}\right)_P\right)_T$$

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

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

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

$$\text{i.) Simplified: } \left(\frac{\partial H}{\partial P} \right)_T - V = -T \left(\frac{\partial V}{\partial T} \right)_P$$

$$D) \text{Pressure dependence of entropy at const. temp: } \left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P = -V\beta$$

$$1.) \text{Total differential parameters: } dS = \frac{C_P}{T} dT - V\beta dP$$

$$\text{i.) Integrate along a reversible path: } \Delta S = \int_{T_i}^{T_f} \frac{C_P}{T} dT - \int_{P_i}^{P_f} V\beta dP$$

i.) applies to single-phase system of pure liq, solid or gas ($T_i, P_i \rightarrow T_f, P_f$) provided no phase change or chemical rxns occur.

6.1 The Gibbs Energy and the Helmholtz energy.

I. State function-Gibbs energy & Helmholtz energy

A) useful to calculate max. work that can be extracted from chemical reaction

B) Clausius inequality (spontaneity): $Tds \geq dq$

i.) only satisfied for reversible process: $Tds \geq du - dw$ or also $-du + dw + Tds \geq 0$
b/c $dq = du - dw$

2.) Nonexpansion work (ex. electrical work): $-du - P_{ext} dV + dw_{nonexp} + Tds \geq 0$

a.) expresses condition of spontaneity in terms of changes in state functions (U, V, S, T) and path-dependent functions ($P_{ext} dV$ & dw_{nonexp})

b.) for isolated sys, $w=0$ & $du=0 \therefore ds \geq 0$

i.) true for systems in equilibrium

C) for isothermal process ($Tds = d(TS)$): $-du + Tds \geq -dw_{exp} - dw_{nonexp}$ or also
 $d(U-TS) \leq dw_{exp} + dw_{nonexp}$

i.) combination of state functions $U-TS$, (units of energy) called a new state function A Helmholtz energy

ii.) abbreviation is $A \therefore dA - dw_{exp} - dw_{nonexp} \leq 0$

iii.) reversible process, max work eqn: $dw_{total} = dw_{exp} + dw_{nonexp} \geq dA$

II. Helmholtz energy ($dT=0$)

A.) const. volume ($dV=0$) $\therefore dw_{exp}=0$ & $dw_{nonexp} = dw_{exp,a} = 0$

i.) spontaneity & equilibrium become $dA \leq 0$

B.) isothermal const. pressure (const. P and T): $PdV = d(PV)$ and $Tds = d(TS)$

i.) Since $H=U+PV \therefore d(H-PV) = d(H-TS) \leq dw_{nonexp}$

a.) combination of state functions $H-TS$, (has units of energy) called new state function G Gibbs energy

i.) abbreviation is $G \therefore$ (isothermal process @ const. P): $dG - dw_{nonexp} \leq 0$

A.) equality holds for reversible process & ΔG energy is a measure of max. nonexpansion work produced in transformation

III. Gibbs energy

A.) Const. P & T when nonexpansion work possible (ex) burning fuel in internal combustion engine): $\Delta G \leq 0$

IV. Using state functions G & A to measure spontaneity than entropy.

A) Clausius inequality: $dS - \frac{dq}{T} \geq 0$

i.) since $dS_{\text{surrounding}} = -dq/T$ then $dS + dS_{\text{surr}} \geq 0$

a.) Introducing G & A, no longer necessary to consider surroundings (only system)
 b.) knowing ΔG & ΔA , enough to predict direction of natural change.

I. Use of G to determine direction of spontaneous change in rxn mixture

A.) Macroscopic change (const. P & T) where no nonexpansion work ~~is~~ possible:

i.) Spontaneity is $\Delta G_R < 0$ so $\Delta G_R = \Delta H_R - T\Delta S_R$

a.) R represents ^{working w/} chemical reaction

b.) 2 contributions to ΔG_R that determine if isothermal chemical transformation is spontaneous:

energetic contribution (ΔH_R) and entropic contribution ($T\Delta S_R$)

i.) entropic contribution to ΔG_R greater for high temp.

ii.) chemical transformation ALWAYS spontaneous if $\Delta H_R < 0$ (exothermic) & $\Delta S_R > 0$

iii.) chemical transformation NEVER spontaneous if $\Delta H_R > 0$ (endothermic) & $\Delta S_R < 0$

iv.) for ^{all} other cases, the magnitudes of ΔH_R & $T\Delta S_R$ determine if spontaneous or not

v.) If forward chemical rxn is NOT spontaneous, then reverse process spontaneous

vi.) If $\Delta G_R = 0$: rxn mixture at equil. & neither direction of change is spontaneous.

B.) ΔG_R depends on conc. of reactants & products & rxn mixture will evolve until $\Delta G_R = 0$ when

@ equil unless rxn rate=0

a.) @ equil: $\exp(-\Delta G_R^\circ / RT)$

C.) Macro. change (const. V & T) where no nonexpansion work possible:

i.) Spontaneity is $\Delta A_R < 0$ so $\Delta A_R = \Delta U_R - T\Delta S_R$

a.) 2 contribution to determine if isothermal chemical transformation is spontaneous:

ΔU_R (energetic contribution) & $T\Delta S_R$ (entropic contribution) $\xrightarrow{\text{to }} \Delta A_R$.

16.2 The Differential Forms of U, H, A and G.

I. State Functions

A.) U & H calculate changes in energy for processes

B.) A & G calculate direction in which processes evolve & max work rxns produce.

C.) Definitions: $H = U + PV$, $A = U - TS$, $G = H - TS = U + PV - TS$

D.) Total differentials: $dU = TdS - PdV$, $dH = TdS - PdV + PdV + VdP = TdS + VdP$,

$dA = TdS - PdV - TdS - SdT = -SdT - PdV$, $dG = TdS + VdP - TdS - SdT = -SdT + VdP$

1.) express internal energy as $U(S, V)$, enthalpy as $H(S, P)$, Helmotz energy as $A(T, V)$, Gibbs energy as $G(T, P)$

2.) Since ⁹ state functions: $dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_V + \left(\frac{\partial U}{\partial V}\right)_S dV$

$$a.) \left(\frac{\partial U}{\partial S}\right)_V = T \text{ & } \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$b.) \left(\frac{\partial H}{\partial S}\right)_P = T \text{ & } \left(\frac{\partial H}{\partial P}\right)_S = V \rightarrow H \text{ inc. if either entropy or pressure of system increase}$$

$$c) \left(\frac{\partial A}{\partial T}\right)_V = -S \quad \& \quad \left(\frac{\partial A}{\partial V}\right)_T = -P$$

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

3.) Since $dU = TdS - PdV$ then $\left(\frac{\partial}{\partial V} \left(\frac{\partial U(S,V)}{\partial S}\right)\right)_V = \left(\frac{\partial}{\partial S} \left(\frac{\partial U(S,V)}{\partial V}\right)\right)_S = -P$

a.) Maxwell Relation: $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$ [refers to partial derivative @ const. S]

b.) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ [refers to partial derivative @ const. S]

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

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

process.

i) Since $dS = \delta q_{rev}/T$, transformation @ const. entropy (S) refers to reversible adiabatic

ii) Maxwell relation derived from U, H, A & G being state functions

iii) useful in transforming obscure partial deriv. in partial deriv. that can be measured.

[6.3] The Dependence of the Gibbs and Helmholtz energies on P, V, and T

I. How A changes with T and V

A.) Eqn: $\left(\frac{\partial A}{\partial T}\right)_V = -S$ and $\left(\frac{\partial A}{\partial V}\right)_T = -P$, S & P are positive

i.) Helmholtz energy of pure substance dec as temp or volume inc.

II. How G changes w/ const. pressure (T & P)

A.) Eqn: $\left(\frac{\partial G}{\partial T}\right)_P = -S$ and $\left(\frac{\partial G}{\partial P}\right)_T = V$

i.) Gibbs energy dec. w/ inc. temp & inc. pressure

B.) Since G a state function, $\Delta_{total} G$ as T & P vary: is the sum of separate contributions.

c.) Maero. change in P at const. T: $\int_{P_0}^P dG = G(T,P) - G^\circ(T,P^\circ) = \int_{P_0}^P VdP'$

i.) initial P: $P^\circ = 1 \text{ bar}$ (standard)

2.) for liq. & solids: $G(T,P) = G^\circ(T,P^\circ) + \int_{P_0}^P VdP' \approx G^\circ(T,P^\circ) + V(P-P^\circ)$

3.) for gas (reversible path & assuming ideal gas): $G(T,P) = G^\circ(T) + \int_{P_0}^P VdP' = G^\circ(T) + \int_{P_0}^P \frac{nRT}{P'} dP' = G^\circ(T) + nRT \ln \frac{P}{P_0}$

a.) Change of G_m w/ P at const. T

b.) $\Delta S = nR \ln(V_f/V_i)$ at const. T

c.) AS $P \rightarrow 0$, $V \rightarrow \infty$. As $V \rightarrow \infty$, $S \rightarrow \infty$ as $P \rightarrow 0$ $\therefore G = H - TS \rightarrow -\infty$

III. Dependence of G on T

A.) Temp dependence of G/T (thermodynamic equil. const. K related to G/T)

1.) Chain Rule: $\left(\frac{\partial[G/T]}{\partial T}\right)_P = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_P + G \frac{d[1/T]}{dT} = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} = -\frac{S}{T} - \frac{G}{T^2}$
 $= -\frac{G+TS}{T^2} = -\frac{H}{T^2} \leftarrow \text{Gibbs-Helmholtz eqn.}$

a.) Used $\left(\frac{\partial G}{\partial T}\right)_P = -S$ & def. $G = H - TS$

b.) Known as Gibbs-Helmholtz eqn b/c: $\frac{d(1/T)}{dT} = -\frac{1}{T^2}$

i.) can be rewritten: $\left(\frac{\partial[G/T]}{\partial[1/T]}\right)_P = \left(\frac{\partial[G/T]}{\partial T}\right)_P \left(\frac{dT}{d[1/T]}\right) = -\frac{H}{T^2} (-T^2) = H$

A.) Replacing G by ΔG & integrating at const. P :

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

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

- 1.) Assumed in second eqn that ΔH indep. of T over interested temp. interval
- 2.) If not the case, integral evaluated numerically using tabulated values of ΔH_f° & temp.-dependent expressions of C_p,m for reactants & prod

T from ΔG no longer arbitrary but related to standard ent.

$\Delta G = \Delta G^\circ + RT \ln \frac{P}{P^\circ}$ gives T when P & ΔG are known.

$$\text{Solving } \Delta G = \Delta G^\circ + \frac{RT^2}{V} \ln \frac{P}{P^\circ} \text{ gives } T = \sqrt{\frac{R\Delta G}{V}}$$

and standard pressure is given, we can substitute into previous standard ent.

(ΔH_f°) standard times few numbers to get ΔG°

$$\Delta G^\circ = \frac{RT^2}{V} \ln \frac{P}{P^\circ} = \frac{RT^2}{V} \ln \frac{P}{P^\circ} = \frac{RT^2}{V} \ln \frac{P}{P^\circ}$$

standard ent. & ΔG° can be each person's addition!

standard enthalpies stored in the most up-to-date tables. If T is 0°C , standard state is $P = 100\text{kPa}$

"New" standard state is $(T, P^\circ) = (298.15\text{K}, 100\text{kPa})$. T times $\ln \frac{P}{P^\circ}$ in standard enthalpies

(enthalpies) and $\Delta G^\circ = \Delta G^\circ + R\ln \frac{P}{P^\circ}$ becomes

$\Delta G^\circ = \Delta G^\circ + RT \ln \frac{P}{P^\circ}$ standard enthalpies of $(T, P^\circ) = (298.15\text{K}, 100\text{kPa})$ plus $2 \cdot \ln \frac{P}{P^\circ}$

$$(\Delta H_f^\circ)_\text{std} = 935 \text{ J/mol} + (298.15 \text{ K}) \cdot 60 \text{ J/mol} \cdot \ln \frac{P}{P^\circ} + 2 \cdot \ln \frac{P}{P^\circ}$$

$$\frac{935 \text{ J/mol} + (298.15 \text{ K}) \cdot 60 \text{ J/mol} \cdot \ln \frac{P}{P^\circ} + 2 \cdot \ln \frac{P}{P^\circ}}{298.15 \text{ K}} = 3.10 \text{ J/K}$$

$T = 298.15 \text{ K}$ has to standardize

$$T = 298.15 \text{ K} \cdot \ln \frac{P}{P^\circ} = 298.15 \text{ K} \cdot 2.30 \cdot 10^{-3} = 0.69 \text{ K}$$

$$T = 298.15 \text{ K} + 0.69 \text{ K} = 298.84 \text{ K}$$

$T = 298.84 \text{ K}$ to standard III

(ΔH_f° at standard & $T = 298.84 \text{ K}$ plus standard ΔG°) \rightarrow to standard ΔG°

$$\frac{\partial}{\partial T} \left(\Delta H_f^\circ + \frac{RT^2}{V} \ln \frac{P}{P^\circ} \right) = \frac{\partial}{\partial T} \left(\Delta H_f^\circ + \frac{RT^2}{V} \ln \frac{P}{P^\circ} \right) = \frac{\partial}{\partial T} \left(\Delta H_f^\circ + \frac{RT^2}{V} \ln \frac{P}{P^\circ} \right) = \frac{\partial}{\partial T} \left(\Delta H_f^\circ + \frac{RT^2}{V} \ln \frac{P}{P^\circ} \right)$$

$$\text{standard enthalpy} \rightarrow \frac{\partial}{\partial T} \left(\Delta H_f^\circ + \frac{RT^2}{V} \ln \frac{P}{P^\circ} \right) = \frac{\partial}{\partial T} \left(\Delta H_f^\circ + \frac{RT^2}{V} \ln \frac{P}{P^\circ} \right)$$

$$\Delta H_f^\circ + \frac{RT^2}{V} \ln \frac{P}{P^\circ} = \frac{\partial}{\partial T} \left(\Delta H_f^\circ + \frac{RT^2}{V} \ln \frac{P}{P^\circ} \right)$$

$\Delta H_f^\circ + \frac{RT^2}{V} \ln \frac{P}{P^\circ} = \frac{\partial}{\partial T} \left(\Delta H_f^\circ + \frac{RT^2}{V} \ln \frac{P}{P^\circ} \right)$ standard enthalpy

$$\Delta H_f^\circ = \frac{\partial}{\partial T} \left(\Delta H_f^\circ + \frac{RT^2}{V} \ln \frac{P}{P^\circ} \right) = \frac{\partial}{\partial T} \left(\Delta H_f^\circ + \frac{RT^2}{V} \ln \frac{P}{P^\circ} \right) = \frac{\partial}{\partial T} \left(\Delta H_f^\circ + \frac{RT^2}{V} \ln \frac{P}{P^\circ} \right)$$