

Chem 531: Problem Set #4**SOLUTIONS**

Due in class: Tues, Oct. 10th

(1) Show that $\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$ and $\left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T$ (note: these should be brief)

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

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

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

$$\therefore \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$$

$$dG = -SdT + VdP$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial H}{\partial P}\right)_S = V$$

$$\therefore \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T$$

(2) (a) Given that $S = f(T, P)$, derive an expression for dS in terms of T and P that is valid for any fluid (i.e., in terms of quantities like C_p , α , and κ).

(b) The coefficient of thermal expansion α of Fe(s) at 25°C is $355 \times 10^{-7} \text{ K}^{-1}$. What is the change in molar entropy of iron when the pressure is raised from 1 to 1000 bar at a constant temperature of 25°C? (The density of iron at 25°C is 7.86 g cm^{-3} .)

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

$$\uparrow$$

$$dS = \frac{dq_{\text{rev}}}{T} = \frac{C_p dT}{T} \quad \text{at const } P.$$

$$\Rightarrow \left(\frac{\partial S}{\partial T} \right)_P = \frac{C_p}{T}$$

for $\left(\frac{\partial S}{\partial P} \right)_T$ a Maxwell relation gives $-\left(\frac{\partial V}{\partial T} \right)_P$



$$dS = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

$$\text{but } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{so} \quad \left(\frac{\partial V}{\partial T} \right)_P = V \alpha$$

$$\therefore dS = \frac{C_p}{T} dT - V \alpha dP$$

$$\textcircled{b} \text{ at const. } T, \quad dS = -V\alpha dP$$

assuming V and α are independent of P ,

$$\Delta S = -V\alpha\Delta P \quad \text{or} \quad \Delta\bar{S} = -\bar{V}\alpha\Delta P$$

$$\bar{V} = \frac{1}{\rho} = \frac{1 \text{ cm}^3}{7.86 \text{ g}} \times \frac{55.847 \text{ g}}{\text{mol}} \times \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^3$$

$$= 7.1052 \times 10^{-6} \text{ m}^3/\text{mol}$$

$$\Delta\bar{S} = -(7.1052 \times 10^{-6})(355 \times 10^{-7})(1000-1) \times \frac{10^5 \text{ Pa}}{1 \text{ bar}}$$

$$= -0.0252 \text{ J K}^{-1} \text{ mol}^{-1}$$

(3) In the thermodynamics of elastic materials, $dA = -SdT + f dL$, where f is the force exerted and L is the stretching displacement. Derive the appropriate Maxwell relation and then use this to obtain an expression for ΔS for isothermal stretching.

$$dA = \left(\frac{\partial A}{\partial T}\right)_L dT + \left(\frac{\partial A}{\partial L}\right)_T dL$$

from Euler's criterion:
$$\left[\frac{\partial}{\partial L} \left(\frac{\partial A}{\partial T}\right)_L\right]_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial A}{\partial L}\right)_T\right]_L$$

but
$$\left(\frac{\partial A}{\partial T}\right)_L = -S$$

and
$$\left(\frac{\partial A}{\partial L}\right)_T = f$$

so
$$-\left(\frac{\partial S}{\partial L}\right)_T = \left(\frac{\partial f}{\partial T}\right)_L$$

for isothermal stretching,

$$\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_L$$

$$dS = -\left(\frac{\partial f}{\partial T}\right)_L dL \quad \text{at } \frac{\text{const.}}{T}$$

$$\text{or } \Delta S = -\int_{L_1}^{L_2} \left(\frac{\partial f}{\partial T}\right)_L dL$$

- (4) Steam is compressed reversibly to liquid water at the boiling point (100°C) and 1 atm. The heat of vaporization of water at 100°C and 1.01325 bar is 2258 J g⁻¹. Calculate w per mole and q per mole and each of the thermodynamic quantities $\Delta\bar{H}$, $\Delta\bar{U}$, $\Delta\bar{G}$, $\Delta\bar{A}$, and $\Delta\bar{S}$. You can assume that the volume of the liquid is negligible compared to that of the gas.

$$\Delta\bar{H} = q_p = -2258 \frac{\text{J}}{\text{g}} \times \frac{18.015 \text{ g}}{\text{mol}} = -40,678 \text{ J/mol}$$

$$\Delta\bar{S} = \frac{\Delta\bar{H}}{T} \text{ since isothermal}$$

$$= \frac{-40,678}{373.15} = -109.01 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta\bar{U} = \Delta\bar{H} - \Delta(PV) \cong \Delta\bar{H} - \Delta n_g RT$$

$$= -40,678 - (-1)(8.3145)(373.15) = -37,575 \text{ J/mol}$$

↑
condensation

$$\Delta\bar{G} = \Delta\bar{H} - T\Delta\bar{S} = -40,678 - (373.15)(-109.01)$$

$$= 0.0 \quad \text{reversible!}$$

for a ~~reversible~~ $w = \Delta U - q = -37,575 - (-40,678)$

$$= 3103 \text{ J/mol}$$

for an isothermal rev. process, $\Delta A = W$

$$\text{so } \Delta A = 3103 \text{ J/mol}$$

(5) When a liquid is compressed its Gibbs energy is increased. The increase in molar Gibbs energy can be calculated using $\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$. What is the change in molar Gibbs energy for liquid water ($\rho = 1.0 \text{ g cm}^{-3}$) when it is compressed from 1 to 1000 bar (assuming \bar{V} is constant)?

from above, $d\bar{G} = \bar{V} dP$ at const. T

$$\Delta \bar{G} = \bar{V} \Delta P$$

$$\begin{aligned}\bar{V} &= \frac{1}{\rho} = \frac{\text{cm}^3}{1.0 \text{ g}} \times \frac{18.02 \text{ g}}{\text{mol}} = 18.02 \text{ cm}^3/\text{mol} \\ &= 1.802 \times 10^{-5} \text{ m}^3/\text{mol}\end{aligned}$$

$$\begin{aligned}\Delta \bar{G} &= (1.802 \times 10^{-5}) (999 \times 10^5 \text{ Pa}) \\ &= 1800 \text{ J/mol}\end{aligned}$$

(6) Starting with the fundamental equation for U , derive the relation $\left(\frac{\partial U}{\partial P}\right)_T = V(\kappa P - \alpha T)$

$$dU = TdS - PdV$$

divide both sides by dP at const. T

$$\left.\frac{dU}{dP}\right|_T = T \left.\frac{dS}{dP}\right|_T - P \left.\frac{dV}{dP}\right|_T$$

$$\begin{array}{l} \text{so } \left(\frac{\partial U}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T - P \left(\frac{\partial V}{\partial P}\right)_T \quad \begin{array}{l} P \quad S \\ T \quad V \end{array} \\ \quad \quad \quad \uparrow \quad \quad \quad \uparrow \\ \quad \quad \quad -\left(\frac{\partial V}{\partial T}\right)_P \quad \quad \quad = -V\kappa \\ \quad \quad \quad \uparrow \\ \quad \quad \quad = -V\alpha \end{array}$$

$$\begin{aligned} \text{so } \left(\frac{\partial U}{\partial P}\right)_T &= -TV\alpha + PV\kappa \\ &= V(\kappa P - \alpha T) \end{aligned}$$