

**Homework 6**

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```
In [7]: #####  
# Futures  
%matplotlib inline  
# from __future__ import unicode_literals  
# from __future__ import print_function  
  
# Generic/Built-in  
import datetime  
import argparse  
  
# Other Libs  
from IPython.display import display, Image  
#  
from sympy import *  
#  
import matplotlib.pyplot as plt  
plt.rc('xtick', labels=14)  
plt.rc('ytick', labels=14)  
#  
import numpy as np  
np.seterr(divide='ignore', invalid='ignore')  
  
# Owned  
# from nostalgia_util import log_utils  
# from nostalgia_util import settings_util  
__authors__ = ["Osamu Katagiri - A01212611@itesm.mx"]  
__copyright__ = "None"  
__credits__ = ["Marcelo Videia - mvidea@itesm.mx"]  
__license__ = "None"  
__status__ = "Under Work"  
#####
```

## Exercise 1 & 2

```
In [4]: display(Image(filename='./directions/1_2.jpg'))
```

1. Read Chapter 2 of “Chemical Thermodynamics of Materials” of Søren and Grande.
2. Read the paper “Gibbs–Helmholtz equation and entropy” by Ernő Keszei.

[1] Stolen, S., Grande, T., & Neil L., A. (2004). Chemical Thermodynamics of Materials - Macroscopic and Microscopic Aspects. (J. W. & S. Inc., Ed.). John Wiley & Sons Ltd.

[2] Keszei, & Erno. (2016). Gibbs – Helmholtz equation and entropy. ChemTexts, 2(15), 15–16.

<https://doi.org/10.1007/s40828-016-0034-4> (<https://doi.org/10.1007/s40828-016-0034-4>)

## Exercise 3

```
In [5]: display(Image(filename='./directions/3.jpg'))
```

3. Starting from the Gibbs–Helmholtz equation, demonstrate that the following equation for the standard free energy at a temperature  $T$  can be derived

$$\Delta G^0(T) = \Delta G^0 \frac{T}{T^0} - \Delta H^0 \left(1 - \frac{T}{T^0}\right)$$

- from [1], equation (1) "is the G-H equation in one of its most substantial form",

$$\left(\frac{\partial(G/T)}{\partial T}\right)_{P,n} = -\frac{H}{T^2}$$

- where

$T$  = temperature

$P$  = pressure

$n$  = composition vector that contains the amount of all the components of the thermodynamic system

$G$  = Gibbs function

$H$  = enthalpy

$$\begin{aligned} d\left(\frac{\partial(G/T)}{\partial T}\right)_{P,n} &= -\frac{H}{T^2} dT \\ \int_{T_i}^{T_f} d\left(\frac{\partial(G/T)}{\partial T}\right)_{P,n} &= \int_{T_i}^{T_f} -\frac{H}{T^2} dT \\ \int_{T_i}^{T_f} d\left(\frac{\partial(G/T)}{\partial T}\right)_{P,n} &= -H \int_{T_i}^{T_f} \frac{1}{T^2} dT \end{aligned}$$

- if  $\partial(G/T) = \Delta G_T$

$$\begin{aligned} \int_{T_i}^{T_f} d\left(\frac{\Delta G_T}{T}\right)_{P,n} &= -H \int_{T_i}^{T_f} \frac{1}{T^2} dT \\ \left(\frac{\Delta G_{T_f}}{T_f}\right)_{P,n} - \left(\frac{\Delta G_{T_i}}{T_i}\right)_{P,n} &= -H \left[\frac{1}{T_i} - \frac{1}{T_f}\right] \end{aligned}$$

- Solve for  $\Delta G_{T_f}$

$$\begin{aligned} \left(\frac{\Delta G_{T_f}}{T_f}\right)_{P,n} &= +\left(\frac{\Delta G_{T_i}}{T_i}\right)_{P,n} - H \left[\frac{1}{T_i} - \frac{1}{T_f}\right] \\ \Delta G_{T_f} &= +\frac{\Delta G_{T_i} T_f}{T_i} - H \left[\frac{T_f}{T_i} - \frac{T_f}{T_f}\right] \\ \Delta G_{T_f} &= \Delta G_{T_i} \frac{T_f}{T_i} - H \left[\frac{T_f}{T_i} - 1\right] \end{aligned}$$

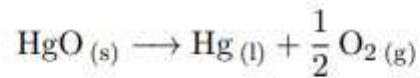
- therefore

$$\Delta G_{T_f} = \Delta G_{T_i} \frac{T_f}{T_i} + H \left[1 - \frac{T_f}{T_i}\right]$$

## Exercise 4

In [6]: `display(Image(filename='./directions/4.jpg'))`

4. Determine the temperature at which the following decomposition reaction



becomes spontaneous.

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ T &= \frac{\Delta H - \Delta G}{S} \\ T &= \frac{90.46 - (-58.43)}{\frac{205.2}{2} + 71.13 - 75.9} K \\ T &= 1.5219 K\end{aligned}$$

- let's obtain the equilibrium temperature (spontaneous reaction)

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S = 0 \\ \Delta H - T\Delta S &= 0 \rightarrow \Delta H = T\Delta S \\ \frac{\Delta H}{\Delta S} &= T\end{aligned}$$

- calculate  $\Delta S$

$$\begin{aligned}\Delta S &= 75.9 + \frac{205.2}{2} - 71.13 \\ \Delta S &= 107.37 \text{ kJ mol}^{-1} \text{ K}^{-1}\end{aligned}$$

- calculate  $\Delta H$

$$\begin{aligned}\Delta H &= 0 + \frac{1}{2}(0) - (-90.46) \\ \Delta H &= 90.46 \text{ kJ mol}^{-1}\end{aligned}$$

- substitute  $\Delta S$  and  $\Delta H$

$$\begin{aligned}T &= \frac{\Delta H}{\Delta S} \\ T &= \frac{90.46}{107.37 \times 10^{-3}} \\ T &= 842.82 K\end{aligned}$$

- therefore

The reaction will be spontaneous at  $T$  less than  $842.82 K$

In [ ]: