Q4001 Thermodynamics of Materials

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', labelsize=14)
plt.rc('ytick', labelsize=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 Videa - 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 Sølen 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)](https://doi.org/10.1007/s40828-016-0034-4)

Exercise 3

In [5]:
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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 subtantial 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 amoun of all the components of the thermodynamic system
  G = Gibbs function
  H = enthalpy

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

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

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

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

$$\int_{T_i}^{T_f} d\left(\frac{\Delta G_T}{T}\right)_{P,n} = -H \int_{T_i}^{T_f} \frac{1}{T^2}\, dT$$

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

- Solve for ΔG_{T_f}

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

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

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

- therefore

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

Exercise 4

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

4. Determine the temperature at which the following decomposition reaction

$$HgO_{(s)} \longrightarrow Hg_{(l)} + \frac{1}{2} O_{2\,(g)}$$

becomes spontaneous.

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

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

$$\Delta G = \Delta H - T\Delta S = 0$$
$$\Delta H - T\Delta S = 0 \rightarrow \Delta H = T\Delta S$$
$$\frac{\Delta H}{\Delta S} = T$$

- calculate ΔS

$$\Delta S = 75.9 + \frac{205.2}{2} - 71.13$$
$$\Delta S = 107.37 kJmol^{-1}K^{-1}$$

- calculate ΔH

$$\Delta H = 0 + \frac{1}{2}(0) - (-90.46)$$
$$\Delta H = 90.46 Jmol^{-1}$$

- substitute ΔS and ΔH

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

- therefore

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

In [ ]: