# Thermodynamics of Materials AD19: Homework 10

**Team:**

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```python
#**********************************************************************#
# Futures
%matplotlib inline
# from __future__ import unicode_literals
# from __future__ import print_function

# Generic/Built-in
import datetime
import argparse

import numpy as np
np.seterr(invalid='ignore')
import pandas as pd
import matplotlib.pyplot as plt
plt.rc('xtick', labelsize=15)
plt.rc('ytick', labelsize=15)
import statsmodels.api as sm

from scipy import special, optimize
from IPython.display import display, Image
from statsmodels.stats.outliers_influence import summary_table
from sklearn.preprocessing import PolynomialFeatures
from sklearn.linear_model import LinearRegression

# Owned
pfont = {'fontname':'Consolas'};
# 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"
#**********************************************************************#
display(Image(filename='./directions/0.jpg'))
```

1. The vapor pressure of neon as a function of temperature is shown in the following table:

| $T/°C$ | $-228.7$ | $-233.6$ | $-240.2$ | $-243.7$ | $-245.7$ | $-247.3$ | $-248.5$ |
|---|---|---|---|---|---|---|---|
| $P/\mathrm{mm\,Hg}$ | 19800 | 10040 | 3170 | 1435 | 816 | 486 | 325 |

   Find the normal boiling point and the evaporation enthalpy and entropy for neon.

2. The vapor pressure of solid NaF varies with temperature as

$$\ln P = -\frac{34450}{T} - 2.01 \ln T + 33.74$$

   and the vapor pressure of liquid NaF varies with temperature as

$$\ln P = -\frac{31090}{T} - 2.52 \ln T + 34.66$$

   (a) The normal boiling temperature of NaF

   (b) The temperature and pressure at the triple point

   (c) The molar enthalpy of evaporation of NaF at its normal boiling temperature

   (d) The molar enthalpy of melting of NaF at the triple point

   (e) The difference between the constant-pressure molar heat capacities of liquid and solid NaF

3. Confirm that the values of the ebulloscopic constants ($K_b$) for water and benzene are 0.51 and 2.63, respectively.

4. Knowing that at the melting temperature of a solution with a solute's mole fraction $x_\mathrm{B}$

$$\mu_\mathrm{A}^\mathrm{s} = \mu_\mathrm{A}^{\mathrm{l},\bullet}$$

   Demonstrate that:

   (a) $\Delta_\mathrm{fus}\mu_\mathrm{A}^\bullet = -RT \ln x_A$

   (b) $\dfrac{\Delta_\mathrm{fus}H^\bullet}{RT^2} = \dfrac{d \ln x_A}{dT}$

   (c) $\dfrac{\Delta_\mathrm{fus}H^\theta}{R} \dfrac{\Delta T_m}{T_m^2} = -\ln x_A$   where   $\Delta T_m = T_m^\circ - T_m^\bullet$

   (d) $\Delta T_m = \dfrac{RT_m^2}{\Delta_\mathrm{fus}H^\theta} x_B$

   (e) $K_f = \dfrac{RT_m^2 M_\mathrm{A}}{\Delta_\mathrm{fus}H^\theta}$ where $M_\mathrm{A}$ is the molar mass of A and $\Delta T_m = K_f m_\mathrm{B}$, in which $m_\mathrm{B}$ is the molality of B.

   Due date: Tuestday, november 5th.

# Exercise 1

The vapour pressure $P$ of neon as a function of temperature T is as follows:

As depicted by Yates [1], the data is a selection of those that were obtained from a fitted expression of the form

$$Log\left(\frac{P}{mmHg}\right) = \frac{0.05223A}{T} + B + CT$$

[1] Yates, P. (2007). Chemical Calculations. Boca Raton: CRC Press, https://doi.org/10.1201/9781420008654 (https://doi.org/10.1201/9781420008654)

```
In [197]:  def fittedExpression_(T, A, B, C):
               res = np.exp(((0.05223*A)/T) + (B) + (C*T))
               return np.log10(res);

           # intialise data of lists.
           data = {'T':[-228.7, -233.6, -240.2, -243.7, -245.7, -247.3, -248.5],
                   'P':[ 19800,  10040,   3170,   1435,    816,    486,    325]}

           # Create DataFrame
           df = pd.DataFrame(data)

           display(df.T)
```

|   | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| T | -228.7 | -233.6 | -240.2 | -243.7 | -245.7 | -247.3 | -248.5 |
| P | 19800.0 | 10040.0 | 3170.0 | 1435.0 | 816.0 | 486.0 | 325.0 |

```
In [198]:  df = df.sort_values(by=['P']);
           P  = df.iloc[:]['P'];
           T  = df.iloc[:]['T'];
           y = np.log10(np.array(P));
           x = np.array(T);

           # constants
           A = -1615.5 #K
           B = 5.69991
           C = 0.0111800 #1/K

           # FIT the Clausius-Clapeyron Equation to the data
           p0 = A, B, C
           results = optimize.curve_fit(fittedExpression_, x, y, p0)
           A = results[0][0];
           B = results[0][1];
           C = results[0][2];
           print('A =', round(A,2))
           print('B =', round(B,2))
           print('C =', round(C,2))

           # PLOT
           scale = 6;
           plt.subplots(figsize=(3*scale, 2*scale));

           # Plot
           T2 = np.linspace(max(x), min(x), 100)
           P2 = fittedExpression_(T2, A, B, C)
           plt.plot(T2, P2, zorder=0)
           plt.scatter(x, y, s=25, label='data', zorder=2);

           # Display plots
           plt.yscale('linear');
           plt.xlabel(r'$T[^\circ C]$', fontsize=24);
           plt.ylabel(r'$log\left(\frac{P}{mmHg}\right)$', fontsize=24);
           plt.title('Figure E1.1', size=24);
           #plt.legend(prop={'size': 18});
           display(plt);
```
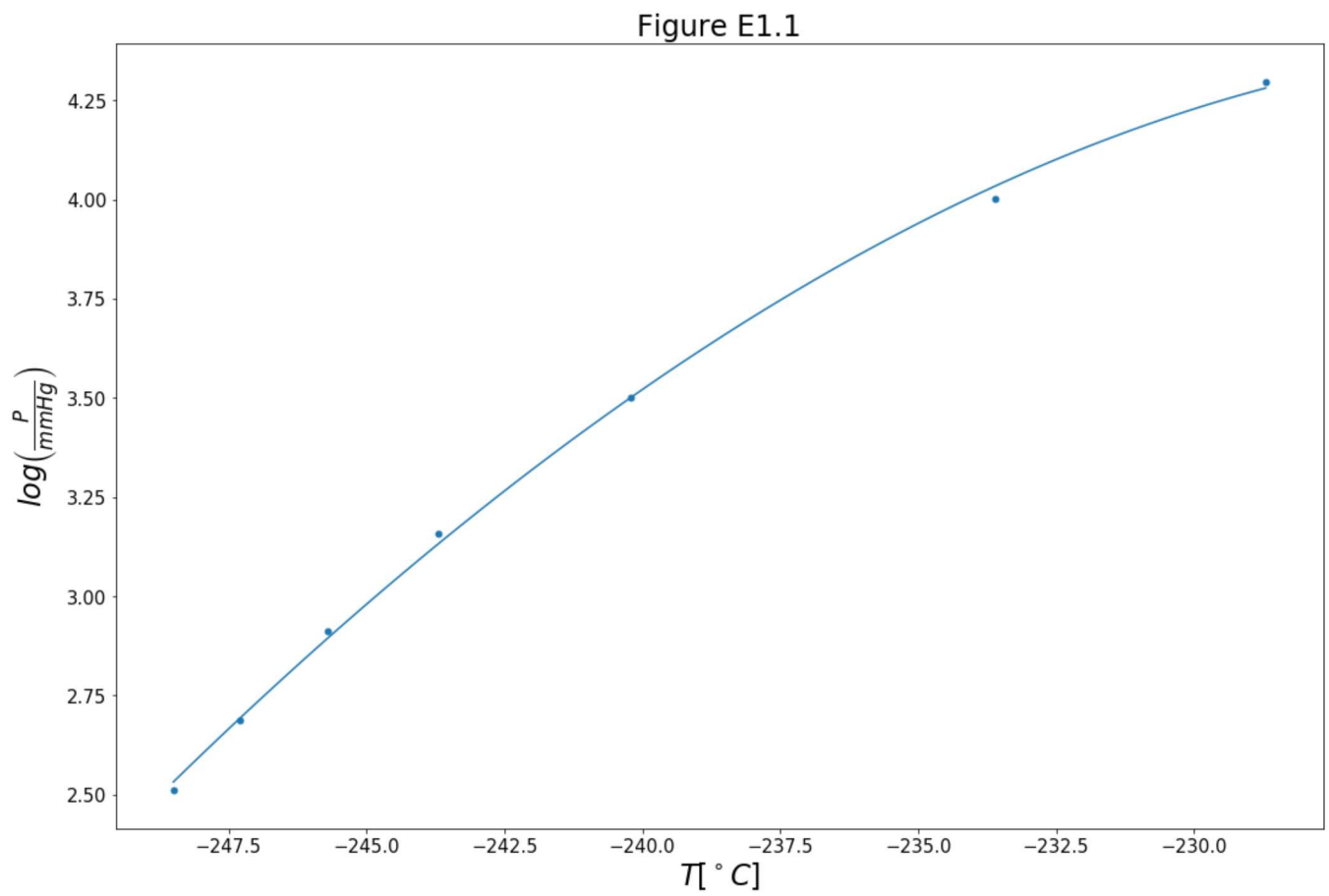
```
A = 1490597.2
B = 710.07
C = 1.57

<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\Anaconda3\\lib\\site-packages\\matp
lotlib\\pyplot.py'>
```



Figure E1.1

At the standard pressure $P^\circ = 1atm$, a liquid boils at its normal boiling point, $T_b$.

Starting from the Clausius–Clapeyron equation

$$ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

If $P_1 = P^\circ, T_1 = T_b, P_2 = P$ and $T_2 = T$

$$ln\left(\frac{P}{P^\circ}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_b} - \frac{1}{T}\right)$$

$$ln\left(\frac{P}{P^\circ}\right) = \frac{\Delta H_{vap}}{RT_b} - \frac{\Delta H_{vap}}{RT}$$

$$ln\left(\frac{P}{P^\circ}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + \frac{\Delta H_{vap}}{RT_b}$$

If $y = mx + c$, then:

$$x = \frac{1}{T}$$

$$y = ln\left(\frac{P}{P^\circ}\right)$$

$$m = -\frac{\Delta H_{vap}}{R}$$

$$c = \frac{\Delta H_{vap}}{RT_b}$$

By ploting $x$ vs. $y$, a straight line will be obtained with gradient $-\frac{\Delta H_{vap}}{R}$ and intercept $\frac{\Delta H_{vap}}{RT_b}$

```
In [220]: df = df.sort_values(by=['P']);
          P  = df.iloc[:]['P'];
          T  = df.iloc[:]['T'];

          # constants
          x = 1/(np.array(T)+273.15);   #1/K
          y = np.log(np.array(P)/760); #<na>

          # Linear Regression
          # X is the independent variable (bivariate in this case)
          X = np.array([x])
          # Y is the dependent data
          Y = y
          # generate a model of polynomial features
          poly = PolynomialFeatures(degree=1)
          # transform the x data for proper fitting (for single variable type it returns,[1,x,x**
          2])
          X_ = poly.fit_transform(X)
          # generate the regression object
          clf = LinearRegression()
          # perform the actual regression
          clf = clf.fit(np.transpose(X), Y)
          c = clf.intercept_
          m = clf.coef_[0]
          print('c =', c)
          print('m =', m)

          # PLOT
          scale = 6;
          plt.subplots(figsize=(3*scale, 2*scale));

          # Plot
          plt.plot(x, m*x + c, label=r'$y = mx + c$', zorder=0)
          plt.scatter(x, y, s=25, zorder=0);

          # Display plots
          plt.yscale('linear');
          plt.xlabel(r'$T[K]$', fontsize=24);
          plt.ylabel(r'$log\left(\frac{P}{mmHg}\right)$', fontsize=24);
          plt.title('Figure E1.2', size=24);
          plt.legend(prop={'size': 18});
          display(plt);
```
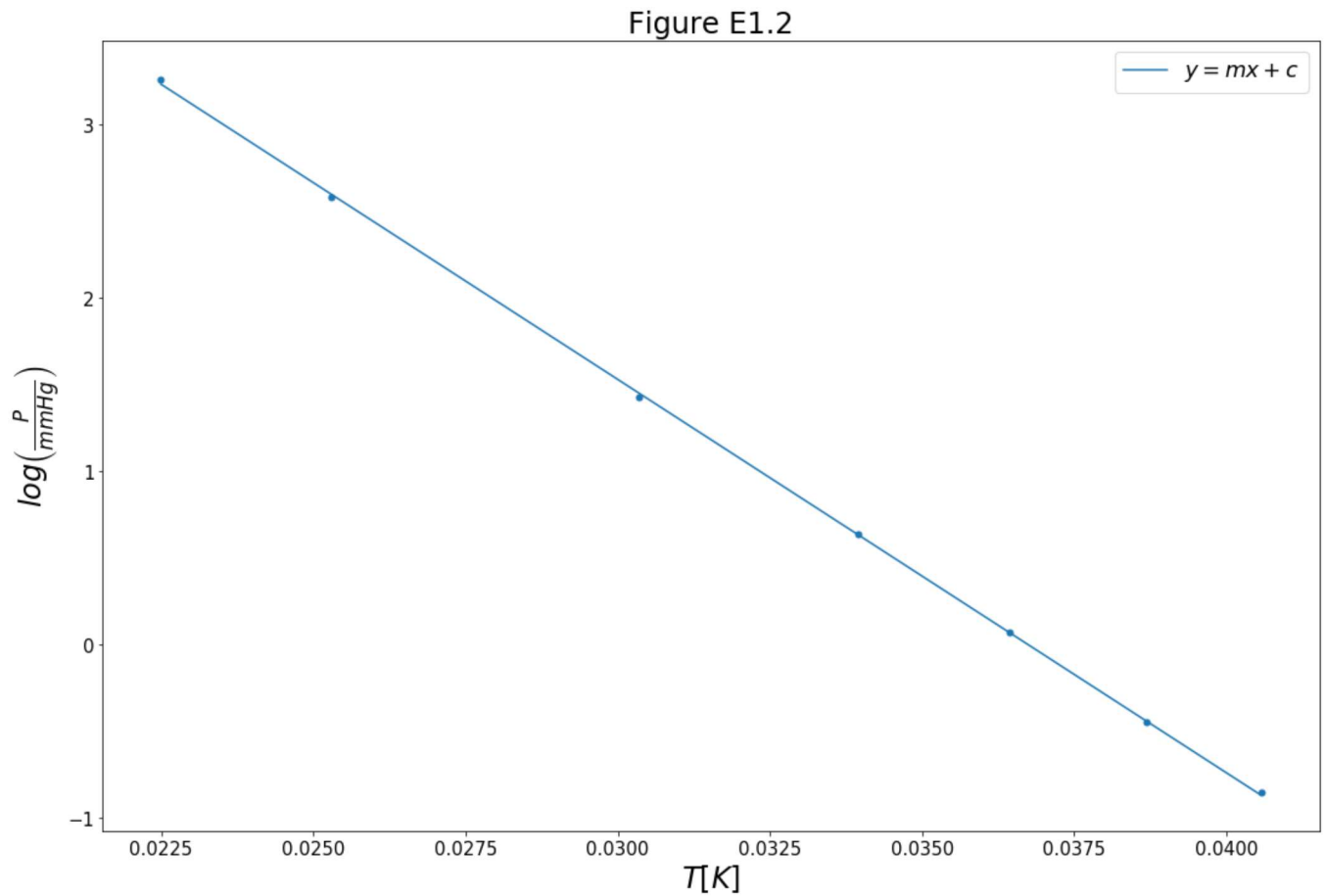
```
c = 8.33476916973932
m = -226.82619930886526
```

```
<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\Anaconda3\\lib\\site-packages\\matp
lotlib\\pyplot.py'>
```



Figure E1.2

In [230]:
```python
R = 8.31446261815324; #J/C mol

H_vap = -(m)*R;
print('H_vap =', round(H_vap,2), 'J/mol')

Tb = H_vap/(c*R);
print('Tb =', round(Tb,2), 'K')

S_vap = H_vap/Tb;
print('S_vap =', round(S_vap,2), 'J/molK')
```

```
H_vap = 1885.94 J/mol
Tb = 27.21 K
S_vap = 69.3 J/molK
```

If $m = -\frac{\Delta H_{vap}}{R}[K]$ then,

$$\Delta H_{vap} = -mR[Jmol^{-1}]$$
$$\Delta H_{vap} = -(-226.83)8.31[Jmol^{-1}]$$

$$\Delta H_{vap} = 1885.94[Jmol^{-1}]$$

If $c = \frac{\Delta H_{vap}}{RT_b}$ then,

$$T_b = \frac{\Delta H_{vap}}{cR}[K]$$
$$T_b = \frac{1885.94}{8.33(8.31)}[K]$$

$$T_b = 27.21[K]$$

The absolute temperature T at which equilibrium occurs in a system is given by

$$T = \frac{\Delta H}{\Delta S}$$

If $T = T_b$, $\Delta H = \Delta H_{vap}$ and $\Delta S = \Delta S_{vap}$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$$
$$\Delta S_{vap} = \frac{1885.94}{27.21}[Jmol^{-1}K^{-1}]$$

$$\Delta S_{vap} = 69.3[Jmol^{-1}K^{-1}]$$

# Exercise 2a

As stated by Gaskell [2], the normal boiling temperature $T_b$ is the temperature at which the vapor pressure of the liquid is $1atm$; hence the following

$$ln(1atm) = -\frac{31090}{T_b} - 2.52lnT_b + 34.66 = 0$$

$$T_b = 2006[K]$$

[2] R. Gaskell, D., & E. Laughlin, D. (2018). Introcuction to the Thermodynamics of Materials. (C. Press, Ed.). Taylor & Francis Group.

# Exercise 2b

The saturated vapor pressures for the solid and liquid phases intersect at the triple point $T_{tp}$; hence the following

$$-\frac{34450}{T_{tp}} - 2.01 ln T_{tp} + 33.74 = -\frac{31090}{T_{tp}} - 2.52 ln T_{tp} + 34.66$$

$$T_{tp} = 1239[K]$$

and

$$P_{tp} = e^{-\frac{34450}{T_{tp}} - 2.01 ln T_{tp} + 33.74}$$

$$P_{tp} = 229.316 \times 10^{-6}[atm]$$

# Exercise 2c

A vapor in equilibrium with a liquid is described by

$$ln P = -\frac{31090}{T} - 2.52 ln T + 34.66$$

$$\frac{d ln P}{dT} = \frac{\Delta H}{RT^2} = \frac{31090}{T^2} - \frac{2.52}{T}$$

$$\Delta H_{vap} = 31090 R - 2.52 RT$$

For $R = 8.3145[J/Cmol]$ and $T = T_b$

$$\Delta H_{vap} = 216466.023[Jmol^{-1}]$$

# Exercise 2d

A vapor in equilibrium with a solid is described by

$$lnP = -\frac{34450}{T} - 2.01lnT + 33.74$$

(as in Exercise 2c ...)

$$\Delta H_{sub} = 34450R - 2.01RT$$

At the triple point,

$$\Delta H_{mel} + \Delta H_{vap} = \Delta H_{sub}$$
$$\Delta H_{mel} = \Delta H_{sub} - \Delta H_{vap}$$
$$\Delta H_{mel} = 34450R - 2.01RT - 31090R + 2.52RT$$
$$\Delta H_{mel} = 3360R + 0.51RT$$

For $R = 8.3145[J/Cmol]$ and $T = T_b$

$$\Delta H_{mel} = 33190[Jmol^{-1}]$$

---

# Exercise 2e

$$\frac{d\Delta H_{mel}}{dT} = \Delta c_P = 0.51R[JK^{-1}]$$

$$\Delta c_P > 0$$

---

# Exercise 3

The ebullioscopic constant $K_b$ is given by:

$$K_b = \frac{RT_{vap}^2 M}{\Delta H_{vap}}$$

where:
$R$ is the gas constant
$T_{vap}$ is the boiling point
$M$ is the molar mass
$\Delta H_{vap}$ is the enthalpy of vaporization

For water: $T_{vap} = 99.9839[°C]$, $M = 18.015[gmol^{-1}]$ and $\Delta H_{vap} = 40.2[kJmol^{-1}]$

$$K_b = \frac{8.3145[J/Cmol](99.9839 + 273.15)[K]^2((18.015/1000)[kgmol^{-1}])}{40.2(1000)[Jmol^{-1}]}$$

$$K_b = 0.5188$$

For benzene: $T_{vap} = 80[°C]$, $M = 78.11[gmol^{-1}]$ and $\Delta H_{vap} = 30.77[kJmol^{-1}]$

$$K_b = \frac{8.3145[J/Cmol](80 + 273.15)[K]^2((78.11/1000)[kgmol^{-1}])}{30.77(1000)[Jmol^{-1}]}$$

$$K_b = 2.6323$$

# Exercise 4a

$$P_A{}^\bullet = x_A P_A \theta$$

...(1)

$$\mu_A{}^{s,\bullet} = \mu_A{}^{s,\circ} + RTx_A$$
$$\mu^{s \to l} = \mu^l - \mu^s$$

from (1)

$$\mu_A{}^{s,\circ} - \mu_A{}^{s,\bullet} = -RTx_A$$

$$\Delta_{fus}\mu_A{}^\bullet = -RTx_A$$

# Exercise 4b

From Exercise 4a

$$\frac{\Delta \mu^{s \to l}}{T} = -R ln x_A$$

...(2)

$$\frac{d \frac{\Delta \mu^{l \to v}}{T}}{dT} = -R \frac{d ln x_A}{dT}$$

Solving $\frac{d \frac{\Delta \mu^{s \to l}}{T}}{dT}$ ...

$$\Delta_{fus} G = \Delta_{fus} H - T \Delta_{fus} S$$
$$\frac{\Delta_{fus} G}{T} = \frac{\Delta_{fus} H}{T} - \Delta_{fus} S$$

...(3)

$$\frac{d \frac{\Delta_{fus} G}{T}}{dT} = -\frac{\Delta_{fus} H}{T^2} = \frac{d \frac{\mu^{s \to l}}{T}}{dT}$$

from (2) and (3)

$$-\frac{\Delta_{fus} H}{T^2} = -R \frac{d ln x_A}{dT}$$

$$\frac{\Delta_{fus} H}{T^2} = R \frac{d ln x_A}{dT}$$

# Exercise 4c

From Exercise 4b, integrate

$$dlnx_A = \frac{\Delta_{fus}H^\theta}{RT^2}dT$$

$$\int_0^{lnx_A} dlnx_A = \frac{\Delta_{fus}H^\theta}{R}\int_{T_m{}^\circ}^{T_b{}^\bullet}\frac{dT}{T^2}$$

$$lnx_A = \frac{\Delta_{fus}H^\theta}{R}\left(\frac{1}{T_m{}^\bullet} - \frac{1}{T_m{}^\circ}\right)$$

If $\Delta T_b = T_m{}^\bullet - T_m{}^\circ$ and $T_m{}^\bullet \approx T_m{}^\circ$

$$lnx_A = -\frac{\Delta_{fus}H^\theta}{R}\frac{T_m{}^\circ - T_m{}^\bullet}{T_m{}^\circ T_m{}^\bullet}$$

...(4)

$$lnx_A = -\frac{\Delta_{fus}H^\theta}{R}\frac{\Delta T_m}{T_m{}^2}$$

$$\frac{\Delta_{fus}H^\theta}{R}\frac{\Delta T_m}{T_m{}^2} = -lnx_A$$

---

# Exercise 4d

From (4), for an dilute solution, $ln(1 - x_B) = -x_B$

$$ln(1 - x_B) = -\frac{\Delta_{fus}H^\theta}{R}\frac{\Delta T_m}{T_m{}^2}$$

$$-x_B = -\frac{\Delta_{fus}H^\theta}{R}\frac{\Delta T_m}{T_m{}^2}$$

...(5)

$$\Delta T_m = \frac{RT_m{}^2}{\Delta_{fus}H^\theta}x_B$$

# Exercise 4e

From (5)

$$\frac{RT_m{}^2}{\Delta_{fus}H^\theta}x_B = K_f m_B$$

If $x_B = \frac{n_B}{n_B+n_A} = \frac{n_B}{n_A}$ for a dilute solution and $m_B = n_B \left[\frac{mol}{L}\right]$

$$\frac{x_B}{m_B} = \frac{\frac{n_B}{n_A}}{n_B} = \frac{1}{n_A} = M_A$$

hence;

$$K_f = \frac{RT_m{}^2 M_A}{\Delta_{fus}H^\theta}$$

In [ ]: