Exam Thermodynamics 2
23 January 2019

Please, hand in your answers to problems 1, 2, 3 and 4 on separate sheets.
Put your name and student number on each sheet.

The examination time is 12:30 until 15:30, **so 3 hours**.
There are 4 problems, each with 4 subproblems, a list of constants and a formulae sheet,
6 pages in total.
All 16 subproblems have equal weight for the final grade.

Problem 1

a) Give a definition **and** *short* description of the following concepts
   -Triple point
   -First order phase transition
   -Regular solution
   -Molality
   -pH

b) Give the characteristic equation for the Gibbs free energy for an open system with two components A and B and electrical work; use it to find a Maxwell relation between the chemical potential of A and E.

c) Give the meaning of all symbols in the following formula as well as a description of its use in thermodynamic problems.

$$X_i = \left(\frac{\partial X}{\partial n_i} \right)_{P,T,n_{j \neq i}}$$

d) At a sublimation (solid to gas) phase transition the entropy increases and as a consequence the number of microstates W increases to W'.
   Use the Boltzmann definition of entropy and the Clapeyron equation to show that

$$W' = W \exp \left[N_g \left(1 - \frac{V_s}{V_g} \right) \right],$$

where V_s and V_g are the volume of the solid and gas respectively and N_g is the number of molecules in the gas.

Problem 2

An electrochemical cell, based on the reaction $2\text{Ag(s)} + \text{Hg}_2\text{Cl}_2\text{(s)} \rightarrow 2\text{Hg(l)} + 2\text{AgCl(s)}$, is kept at a constant temperature of $T = 298$ K and at 1 bar.
The ElectroMotive Force (EMF) of the cell is 0.046 V at the given temperature and pressure.
For these conditions the reaction enthalpy is $\Delta_r H = 11.08$ kJ/mol.
The change in volume during the reaction can be considered as negligible.
The cell delivers a current to an external circuit.

a) Give the chemical equations for the half cell reactions.

b) Calculate the reaction Gibbs free energy $\Delta_r G$ (in J/mol Hg_2Cl_2) at 298 K.

c) Calculate the heat of the cell (in J/mol Hg_2Cl_2) in case the reaction proceeds reversibly.

d) Calculate the temperature coefficient $\left(\frac{\partial E}{\partial T} \right)_{P,q}$ of the EMF of the cell.

Problem 3

We consider the chiral compounds methylsuccinic acid and isopropylsuccinic acid.
We will use the following abbreviations for three of the four enantiomers:
R-MSA for (R)-methylsuccinic acid,
S-IPSA for (S)-isopropylsuccinic acid and
R-IPSA for (R)-isopropylsuccinic acid.
R-MSA and S-IPSA form a so-called quasi-racemic compound (R-MSA/S-IPSA)(s),
S-IPSA and R-IPSA form a racemic compound (S-IPSA/R-IPSA)(s) and
R-IPSA and R-MSA show a eutectic phase behaviour.
The phase diagram of the three combinations at $P = P^{\ominus}$ is given in Figure 1.
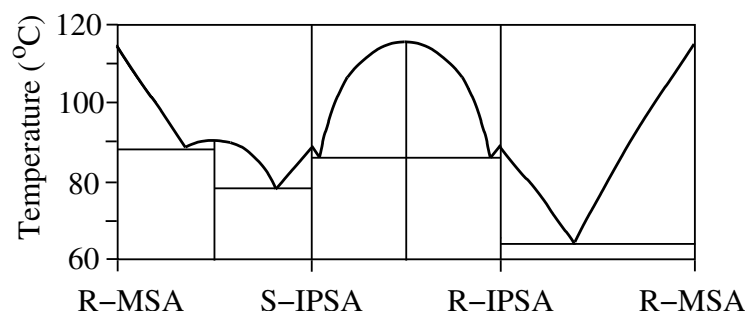

Figure 1: The phase diagram of the three combinations. The vertical lines represent the pure enantiomers as indicated; the horizontal axis represents the corresponding mole fractions, running three times from $x = 0$ to $x = 1$ for S-IPSA, R-IPSA and R-MSA, respectively. Eutectic compositions are present for $x_e = 0.35, 0.81, 0.05$ and 0.29.

Further data are
T_{fus}(R-MSA) = 114.0 °C,
T_{fus}(S-IPSA) = 88.5 °C,
T_{fus}(S-IPSA/R-IPSA) = 115.0 °C,
the eutectic temperature in the (R-MSA, S-IPSA) phase diagram is $T_e = 88.0$ °C at $x_e = 0.35$,
the eutectic temperature in the (S-IPSA, R-IPSA) phase diagram is $T_e = 85.5$ °C,
the eutectic temperature in the (R-IPSA, R-MSA) phase diagram is $T_e = 64.0$ °C,
$\Delta_{\text{fus}} H^{\ominus}$(S-IPSA) = 18.2 kJ/mol and
$\Delta_{\text{fus}} H^{\ominus}$(S-IPSA/R-IPSA) = 250.5 kJ/mol and is considered independent of the temperature.

a) The phase diagram is also present on a separate sheet.
   Use this sheet to indicate the two-phase regions by hatching these areas in ALL regions of the phase diagram AND specify the phases present in all regions of ONLY the (R-MSA, S-IPSA) diagram (e.g.: R-MSA(s) + (R-MSA, S-IPSA)(l)).
   Advise: add the further data given above to the diagram.
   Hand in this sheet together with your other results.

b) The phase boundary line in the (R-MSA, S-IPSA) diagram starting from pure R-MSA can be considered as linear.
   Calculate $\Delta_{\text{fus}} H^{\ominus}$(R-MSA).

c) The liquid phase at $x = 0.70$ in the (R-IPSA, R-MSA) diagram is cooled down to the eutectic temperature.
   Calculate the relative amounts $n(\text{l})/n(\text{s})$ of the liquid and solid phases present at this temperature.

d) Determine the activity coefficient of the racemic compound γ(S-IPSA/R-IPSA)(l) in the liquid phase at the eutectic temperature in the (S-IPSA, R-IPSA) phase diagram.

Problem 4

At standard pressure dimethylsulfoxide ($(CH_3)_2SO$, DMSO) is a liquid at room temperature. Some further data for DMSO are:

$M = 78.13$ g mol^{-1}

$\rho = 1.1004$ g cm^{-3} at 298 K

$T_{fus} = 292$ K

$T_{vap} = 462.15$ K

$\Delta_{vap}H = 42.70$ kJ/mol

The temperature dependence of the vapour pressure P^* of the liquid is given by

$$^{10}\log P^* = A + \frac{B}{T} + C^{10}\log T + DT + ET^2,$$

where T is in Kelvin, P^* is in Torr, and

$A = 45.465$ Torr,

$B = -4.044 \cdot 10^3$ Torr K,

$C = -1.321 \cdot 10^1$ Torr,

$D = 1.098 \cdot 10^{-7}$ Torr K^{-1} and

$E = 6.415 \cdot 10^{-6}$ Torr K^{-2}.

The temperature dependence of the surface tension for the liquid-vapour interface is given by

$$\gamma^{lg} = G\left(1 - \frac{T}{T_c}\right)^n, \quad \text{where}$$

$G = 93.260$ mN/m,

$T_c = 726.00$ K and

$n = 1.4300$,

resulting at $T = 298$ K in the value $\gamma^{lg} = 43.8$ mN/m.

a) Calculate the vapour pressure of a spherical liquid droplet of DMSO with a diameter of 1 μm at 298 K.

Next we consider a bulk liquid of DMSO at constant pressure ($P = P^{\ominus}$), in which a spherical DMSO vapour bubble, with a radius r, is present. The boiling temperature of the liquid is then dependent on the bubble radius r. This dependence is in good approximation given by

$$T_{vap}(r) = \frac{T_{vap}}{1 - \frac{RT_{vap}}{\Delta_{vap}H}\ln\left[1 + \frac{2\gamma}{Pr}\right]},$$

where T_{vap} is the boiling temperature for $r = \infty$.

b) Calculate the boiling temperature of liquid DMSO for a vapour bubble diameter of 1 μm.

c) The result of the former part is that it is possible to have a superheated liquid of DMSO. In reality the maximum achievable superheating is limited.
   Discuss briefly what diminishes the superheating in practice.

d) Use the equilibrium condition for the liquid-vapour coexistence situation to find the expression for $T_{vap}(r)$ given above.
   Hint: Consider the vapour to behave as a perfect gas and assume that $\Delta_{vap}H$ as well as the surface tension are independent of the temperature and equal to their values at T_{vap}.

List of constants

Elementary charge	e	$1.602 \cdot 10^{-19}$ C
Faraday's constant	F	$9.648 \cdot 10^{4}$ Cmol^{-1}
Vacuum dielectric constant	ϵ_0	$8.854 \cdot 10^{-12}$ C^{2}J^{-1}m^{-1}
Boltzmann's constant	k	$1.381 \cdot 10^{-23}$ JK^{-1}
Planck's constant	h	$6.626 \cdot 10^{-34}$ Js
Bohr magneton	μ_B	$9.274 \cdot 10^{-24}$ JT^{-1}
Atomic mass constant	m_u	$1.661 \cdot 10^{-27}$ kg
Amadeo Avogadro di Quaregna e Ceretto's constant	N_A	$6.022 \cdot 10^{23}$ mol^{-1}
Gas constant	R	8.314 JK^{-1}mol^{-1}
Free fall acceleration	g	9.807 ms^{-2}
Unit of energy		1 cal = 4.184 J
Standard pressure	$P^{\ominus}$	1 bar = 10^5 Nm^{-2} = 0.9869 atm = 750 Torr

Formulae Thermodynamics (1)

$$PV = nRT = NkT$$

$$U = \frac{3}{2}nRT = \frac{3}{2}NkT$$

$$\Delta U = W + Q$$

$$\mathrm{d}W = -P_{ext.}\mathrm{d}V + \mathrm{d}W' \quad \text{and} \quad \mathrm{d}W'_{max} = (\mathrm{d}G)_{P,T}$$

$$\mathrm{d}Q|_P = C_P\mathrm{d}T \quad \text{and} \quad \mathrm{d}Q|_V = C_V\mathrm{d}T$$

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$$

$$\mathrm{d}S = \frac{\mathrm{d}Q^{rev}}{T} \geq \frac{\mathrm{d}Q}{T}$$

$$\mathrm{d}S_{tot} = \mathrm{d}S + \mathrm{d}S_{omg} \geq 0$$

$$\mathrm{d}U = -P\mathrm{d}V + T\mathrm{d}S + \sum_i \mu_i \mathrm{d}n_i$$

$$H = U + PV$$

$$\mathrm{d}H = V\mathrm{d}P + T\mathrm{d}S + \sum_i \mu_i \mathrm{d}n_i$$

$$A = U - TS$$

$$\mathrm{d}A = -P\mathrm{d}V - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$$

$$G = H - TS$$

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \Delta_r G^\ominus + RT \ln Q, \quad \text{where} \quad Q = \prod_i a_i^{\nu_i}$$

$$RT \ln K = -\Delta_r G^\ominus$$

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q \quad \text{and} \quad \mathrm{d}W' = E\mathrm{d}q \quad \text{and} \quad E = IR \quad \text{and} \quad P = EI$$

$$\mu_i = \mu_i^\ominus + RT \ln a_i = \mu_i^\ominus + RT \ln \frac{P_i}{P^\ominus}$$

$$G_{P,T} = \sum_i \mu_i n_i$$

$$\sum_j n_j \mathrm{d}\mu_j = 0$$

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{\mathrm{trs}}H}\right) x_B$$

$$\Delta S = -nR\left(x_A \ln x_A + x_B \ln x_B\right)$$

$$\Pi = [B]RT = \frac{n_B}{V}RT$$

$$S = k \ln W$$

$$\frac{n_i}{N} = \frac{\exp \frac{-\epsilon_i}{kT}}{q}, \quad \text{where} \quad q = \sum_i \exp \frac{-\epsilon_i}{kT} \quad \text{and} \quad <X> = N <x> = N \sum_i x_i \frac{n_i}{N}$$

Formulae Thermodynamics 2

$$\left(\frac{\partial V}{\partial T}\right)_{P,W',n_i} = -\left(\frac{\partial S}{\partial P}\right)_{T,W',n_i}$$

$$X_i = \left(\frac{\partial X}{\partial n_i}\right)_{P,T,n_{j\neq i}}$$

$$\sum_j n_j \mathrm{d}\mu_j = 0$$

$$P_j = x_j P_j^*$$

$$P_j = y_j P$$

$$P_B = x_B K_B$$

$$\left(\frac{\partial \mu_\beta}{\partial P}\right)_T - \left(\frac{\partial \mu_\alpha}{\partial P}\right)_T = \Delta_{\mathrm{trs}} V$$

$$\left(\frac{\partial \mu_\beta}{\partial T}\right)_P - \left(\frac{\partial \mu_\alpha}{\partial T}\right)_P = -\Delta_{\mathrm{trs}} S$$

$$P = P^* \exp\left(\frac{V_m \Delta P}{RT}\right)$$

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{trs}} S}{\Delta_{\mathrm{trs}} V} = \frac{\Delta_{\mathrm{trs}} H}{T \Delta_{\mathrm{trs}} V}$$

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T} \approx \frac{\Delta_{\mathrm{trs}} H}{RT^2}$$

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{\mathrm{trs}} H}\right) x_B \qquad \ln x_B = \frac{\Delta_{\mathrm{fus}} H}{R}\left[\frac{1}{T_{\mathrm{fus}}} - \frac{1}{T}\right]$$

$$\mu = \mu^{\ominus} + RT \ln a = \mu^{\ominus} + RT \ln x + RT \ln \gamma$$

$$\mu = \mu^{\ominus} + RT \ln a = \mu^{\ominus} + RT \ln \frac{b}{b^{\ominus}} + RT \ln \gamma$$

$$F = C - P + 2$$

$$n_\alpha l_\alpha = n_\beta l_\beta$$

$$\Delta_{\mathrm{solv}} G^{\ominus} = -\frac{z_i^2 e^2 N_A}{8\pi\epsilon_0 r_i}\left(1 - \frac{1}{\epsilon_r}\right)$$

$$\gamma_\pm = \left(\gamma_+^p \gamma_-^q\right)^{\frac{1}{p+q}}$$

$$\log \gamma_\pm = -|z_+ z_-| A\sqrt{I}$$

$$I = \frac{1}{2}\sum_i z_i^2 \frac{b_i}{b^{\ominus}}$$

$$A = \frac{F^3}{4\pi N_A \ln 10}\left(\frac{\rho b^{\ominus}}{2\epsilon^3 R^3 T^3}\right)^{\frac{1}{2}}$$

$$P_{in} = P_{out} + \frac{2\gamma}{r} \qquad P = \rho g h \qquad w_{ad} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl} \qquad \gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \Theta_c$$
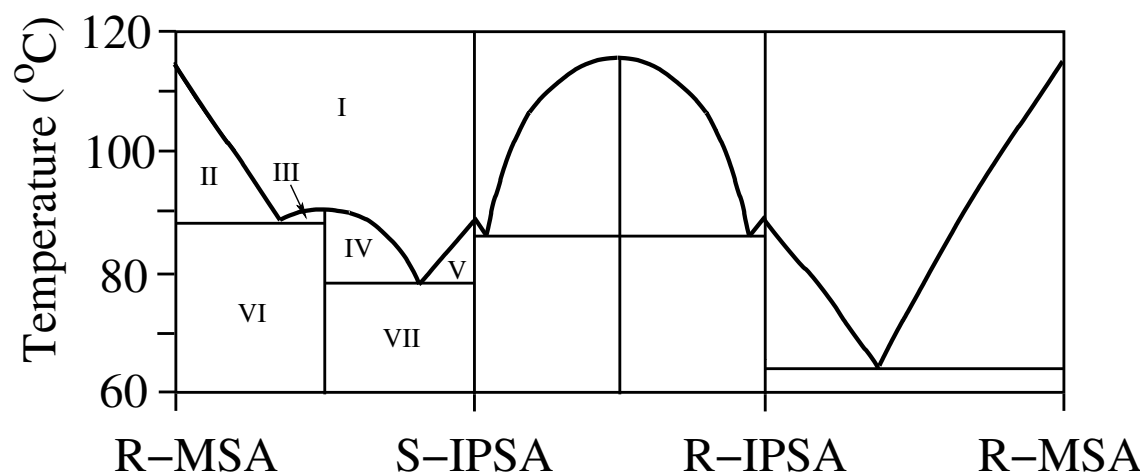
Use this sheet to indicate the two-phase regions by hatching these areas in ALL regions of the phase diagram AND specify the phases present in the regions I-VII of ONLY the (R-MSA, S-IPSA) diagram; e.g.: R-MSA(s) + (R-MSA, S-IPSA)(l) (problem 3a).
Hand in this sheet together with your other results.

Name:
Student no.:
FINAL/DRAFT (please, indicate)

THE FOLLOWING DIAGRAM CAN BE USED AS WELL IN CASE YOU RECONSIDER YOUR RESULT. INDICATE FINAL/DRAFT.

Name:
Student no.:
FINAL/DRAFT (please, indicate)