

## Problem set 5 – Phase and Chemical Equilibrium

### Exercise Maths 5

- Show that  $\int_{T_1}^{T_2} \frac{A}{T^2} dT = -A \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$ , where  $A$  is a constant,
- By differentiating  $\ln p$  with respect to  $p$ , show that  $\frac{1}{p} dp = d \ln p$ .
- Determine  $\int_{p_1}^{p_2} d \ln p$ .

The Clausius-Clapeyron equation (in integrated form) is given by

$$\ln \frac{p}{p^\ominus} = -\frac{\Delta_{trs}H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right),$$

where  $T_1$  is the transition temperature at  $p^\ominus$  (and thus constant). Rearrange the Clausius-Clapeyron equation to show that in a plot of  $\ln(p/p^\ominus)$  as a function of  $\frac{1}{T_2}$  (hence,  $T_2$  is the ‘running variable’)

- the slope is given by  $-\frac{\Delta_{trs}H}{R}$ ,
- and the intercept is  $\frac{\Delta_{trs}H}{RT_1}$ .

### Exercise 21

- Starting from the Gibbs-Duhem equation,  $d\mu = -S_m dT + V_m dP$ , derive the Clapeyron equation,

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}. \quad (1)$$

- Sketch the phase diagram of water near the triple point and label the phases, indicate the triple and critical points, and discuss the slopes of the phase boundaries with reference to the Clapeyron equation.
- Why is the solid-liquid boundary negative and the solid-gas boundary always steeper than the liquid-gas boundary?
- Stating any approximations, derive the Clausius-Clapeyron equation for the vapour pressure of a liquid

$$\frac{d \ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}.$$

### Exercise 22

- The enthalpy of vaporization of water is  $44.0 \text{ kJ mol}^{-1}$ . Estimate the vapour pressure of water at  $120^\circ \text{C}$ .
- Show that the Clapeyron equation for an equilibrium between a solid and its liquid is given by

$$p_2 - p_1 = \frac{\Delta_{fus}H}{\Delta_{fus}V} \ln \frac{T_2}{T_1}.$$

The enthalpy of fusion (melting) is  $6.01 \text{ kJ mol}^{-1}$ , the vapour pressure at the triple point is  $533.29 \text{ Pa}$  and the mass densities of ice and water at  $0^\circ \text{C}$  are  $0.917 \text{ g cm}^{-3}$  and  $1.0 \text{ g cm}^{-3}$  respectively. The molar mass of water is  $18 \text{ g mol}^{-1}$ .

- Calculate the difference between the melting point of ice at  $1 \text{ atm}$  pressure and at the temperature of the triple point of water and comment on the small value you (should) obtain.

## Exercise 23

The vapour pressure of CO<sub>2</sub> at different temperatures are as follows:

$T$ (K)	$p$ (bar)
186	0.526
196	1.132
206	2.447
226	7.605
236	11.065
246	15.579

- Determine  $\Delta_{\text{vap}}H$  and  $\Delta_{\text{sub}}H$  of CO<sub>2</sub> in this temperature range.
- Determine  $\Delta_{\text{fus}}H$  of CO<sub>2</sub>.

## Exercise 24

The reaction Gibbs energy is defined by

$$\Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{T,p} . \quad (2)$$

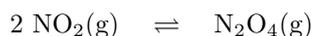
- Sketch a graph of  $G_{T,p}$  (Gibbs energy at constant  $T$  and  $p$ ) vs.  $\xi$  (extent of the reaction) and
  - explain the shape of the curve,
  - indicate where the forward and backward reactions are spontaneous,
  - and where equilibrium is reached.

The standard enthalpy and entropy of formation of methane (CH<sub>4</sub>) at 298 K are given by  $\Delta_f H^\ominus(\text{CH}_4, \text{g}) = -74.85$  kJ/mol and  $\Delta_f S^\ominus(\text{CH}_4, \text{g}) = -80.67$  J/molK.

- Calculate the equilibrium constant at 298 K for the decomposition of methane CH<sub>4</sub>(g) into the elements H<sub>2</sub>(g) and graphite C(s).
- What does this result imply for the position of the equilibrium (to the left hand side or the right hand side of the reaction)?
- Write down the expression for the equilibrium constant  $K_p$  in terms of the partial pressures for the decomposition reaction of methane.

## Exercise 25

NO<sub>2</sub> is in equilibrium with its dimer at room temperature:



Use the following data for the (partial) pressures of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> at equilibrium

	$p(\text{NO}_2)$ (bar)	$p(\text{N}_2\text{O}_4)$ (bar)
298 K	0.061	0.031

to calculate:

- the equilibrium constant for the reaction, and
- the standard molar Gibbs free energy.