

Problem set 4 – Gibbs and Helmholtz free energies

Exercise Maths 4

- With $f = f(x)$, use the product rule (or otherwise) to show that $\left(\frac{\partial(f/x)}{\partial x}\right)_y = \frac{1}{x} \left(\frac{\partial f}{\partial x}\right)_y - \left(\frac{f}{x^2}\right)$.
- Write down the total differential of $z(x, y)$ in terms of the partial derivatives.
- Given that $z(x, y) = x^4 e^{3y}$. Compute the partial derivatives $\left(\frac{\partial z}{\partial x}\right)_y$ and $\left(\frac{\partial z}{\partial y}\right)_x$.
- Use your answer from part c) to show that $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$ (as is the case when z is a state function).

Exercise 16

Consider 1.0 mole of an atomic perfect gas at an initial temperature of 25°C and pressure of 5.0 bar.

- Calculate the values for the following quantities for an isothermal and reversible expansion to a final pressure of 1.0 bar:
 - the final temperature,
 - the work done,
 - the change in internal energy,
 - the change in heat ,
 - the entropy change,
 - the change in the Helmholtz free energy and
 - the change in the Gibbs free energy.
- Discuss (without calculation) whether you expect a different answer for all quantities listed in part a) for an isothermal expansion from an initial pressure of $p = 5$ bar to a final pressure of $p = 1$ bar, but now against a constant external pressure of 1.0 bar. Note that this is an *irreversible* process.
- Determine the values of the quantities listed in part a) for the irreversible process.

Exercise 17

- Starting from the First Law of Thermodynamics (including expansion and chemical work), the thermodynamic definition of the entropy and the definition of the Gibbs free energy (G), show that the fundamental equation for the Gibbs free energy is given by

$$dG = -SdT + Vdp + \mu dn.$$

- Write down the total differential for $G(T, p, n)$ and compare it to the answer in part a) to show that the temperature variation of the Gibbs free energy is given by

$$\left(\frac{\partial G}{\partial T}\right)_{p,n} = -S.$$

- The temperature variation of G in terms of the enthalpy H is given by the Gibbs-Helmholtz equation

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

Derive the Gibbs-Helmholtz equation using the answer to part b) and the definition of the Gibbs free energy ($G = H - TS$).

Exercise 18

At $T = 298$ K the enthalpy change of the graphite (G) \rightarrow diamond (D) phase transition is $\Delta_r H = 1.8961$ kJ mol⁻¹ and the entropy change is $\Delta_r S = -3.2552$ J K⁻¹ mol⁻¹.

- Determine whether the graphite \rightarrow diamond transition takes place spontaneously at 25°C?
- Which direction ($G \rightarrow D$ or $D \rightarrow G$) is favoured by a rise in temperature?
- Starting from the fundamental equation for G , derive an expression for the pressure dependence of G assuming that V is independent of the pressure. Write down the resulting expressions for both diamond, $G_D(p)$, and graphite, $G_G(p)$.
- For the $G \rightarrow D$ transition, $\Delta V = V_D - V_G = -1.92$ cm³mol⁻¹, and $\Delta_r G^\ominus = 2.9$ kJ mol⁻¹. At what pressure would diamond become stable at 298 K?

Exercise 19

- From the fundamental equation for the Helmholtz free energy, derive the following Maxwell-relation

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial p}{\partial T}\right)_{V,n}.$$

- Use the Maxwell-relation from part a) to derive an expression for the entropy change for an isothermal expansion of n moles of a perfect monatomic gas from volume V_1 to volume $V_2 = 2V_1$.
Note that the same expression was obtained in Exercise 13 (problem set 3), but then starting from the thermodynamic definition of the entropy.

Exercise 20

Consider a system consisting of 1 mole sodium, Na, at standard pressure p^\ominus . In the table below a number of thermodynamic parameters is given.

	T_{fus}	$\Delta_{fus}H$	T_{vap}	$\Delta_{vap}H$
Na	371.0 K	2.601 kJ/mol	1156 K	98.01 kJ/mol

The heat capacity at constant pressure for all phases is given by (T is the temperature in K)

$$C_p(\text{J/molK}) = A + BT + CT^2,$$

in which the parameters A , B and C , for temperatures $10 \text{ K} \leq T \leq 1500 \text{ K}$, in the three phases s(olid), l(iquid) and g(as) are given in the table below

Na	$A(\text{J/molK})$	$B(\text{J/molK}^2)$	$C(\text{J/molK}^3)$
solid	72.6	$-9.49 \cdot 10^{-3}$	$-731 \cdot 10^{-6}$
liquid	40.3	$-28.2 \cdot 10^{-3}$	$20.7 \cdot 10^{-6}$
gas	20.8	$-0.277 \cdot 10^{-3}$	$-0.392 \cdot 10^{-6}$

- At very high temperature the system behaves like an atomic perfect gas. What are the values of A , B and C in that case?

- b) Which of the following quantities have the same value for both phases (melt and solid) at constant pressure, at $T = T_{fus}$, where the melt and the solid are in equilibrium?
- the entropy,
 - the chemical potential,
 - the enthalpy,
 - the Gibbs free energy,
 - the Helmholtz free energy.
- c) Calculate the entropy change $\Delta_{vap}S$ at the evaporation temperature T_{vap} .
- d) Calculate the entropy of this system at 1000 K; you can neglect the contributions for $T < 10$ K.