

FINAL EXAM
Chemical Thermodynamics

(AESB2220)

27 January 2015

14:00–17:00 uur

Docent: W. Smith

Name:

Student number Delft:

- This test consists of four questions
- Make each problem on a separate sheet of paper
- The point distribution is given for each question
- The maximum points achievable is 100
- This exam counts for 40% of your final grade

- This is a closed-book exam.
- Answer the questions as possible to the method / implementation / consideration structure
- Course material may not be consulted, except the attached formula sheet
- A simple or scientific calculator is permitted; a graphic (programmable) calculator is not allowed.
- Indicate on each sheet name and number the pages
- Clearly identify the number and part of each question.
- Make this exam in blue or black ink. No pencil!
- Include this sheet with the submitted assignments

Question 1: Multiple choice questions (20 points)

(20pt max, each question is worth 1 point)

Please use the attached answer sheet to fill in the answers for the individual sub-questions

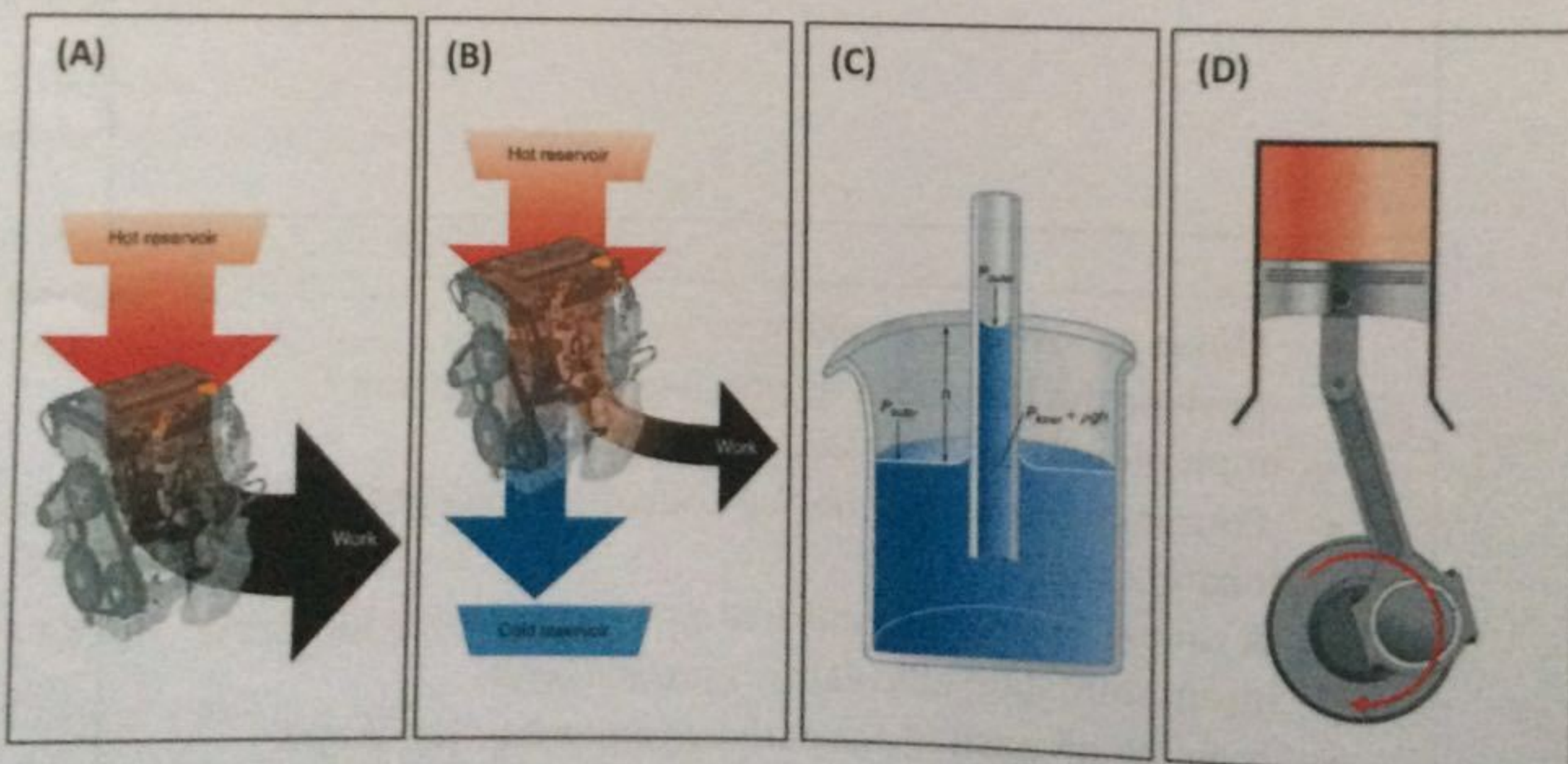
Question 1: Which of the following is an example of the zeroth (0th) law of thermodynamics?

- A The entropy of the universe is always increasing
- B The entropy of the universe is always decreasing
- C A thermometer measuring the same temperature for two systems
- D Two liquids coming into thermal contact and both approaching the same temperature over time

Question 2: Which of the following is an example of the first (1st) law of thermodynamics?

- A A hot beverage staying hot over time
- B A cool beverage staying cool over time
- C The internal energy of a system decreasing over time
- D An ice skater moving at a constant speed over ice (a frictionless surface)

Question 3: Which of the following is an example of the second (2nd) law of thermodynamics?



Question 4: Which of the following is an example of the third (3rd) law of thermodynamics?

- A $\Delta S = 0$ at $T = 0$ K
- B $\Delta S = 0$ at $T = 273$ K
- C $\Delta G = 0$ at $T = 0$ K
- D $\Delta S = 0$ when $\Delta G = 0$

Question 5: In a phase diagram, if $V_m^{\text{liquid}} > V_m^{\text{solid}}$, and the pressure is increased, the change of the melting point temperature will:

- A increase
- B decrease
- C Stay the same
- D become the boiling point, i.e. sublimation will occur

Question 6: In the van der Waals equation, the constant, a , is used to describe:

- A the Born repulsion
- B van der Waals attraction
- C Lorentz repulsion
- D Faraday attraction

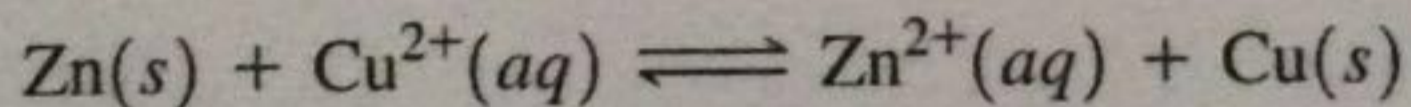
Question 7: Which of the following is a state function:

- A work (w)
- B heat (q)
- C volume (V)
- D internal energy (U)

Question 8: For a reversible adiabatic expansion, the following holds true:

- A $q=0$, T will decrease
- B $q=W$, T will increase
- C $q=0$, T will increase
- D $q=W$, T will decrease

Question 9: The abbreviated reaction equation for the Daniell cell



Can be written as the following:

- A $\text{Zn}^{2+}(aq) | \text{Zn}(s) || \text{Cu}(s) | \text{Cu}^{2+}(aq)$
- B $\text{Cu}(s) | \text{Cu}^{2+}(aq) || \text{Zn}^{2+}(aq) | \text{Zn}(s)$
- C $\text{Zn}(s) | \text{Cu}^{2+}(aq) || \text{Zn}^{2+}(aq) | \text{Cu}(s)$
- D $\text{Zn}(s) | \text{ZnSO}_4(aq) || \text{CuSO}_4(aq) | \text{Cu}(s)$

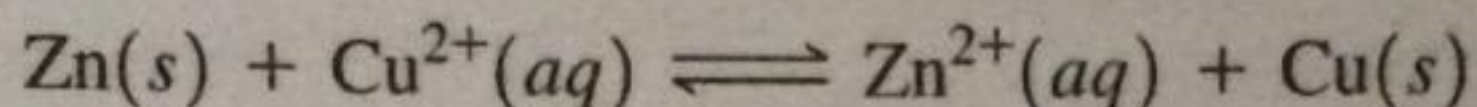
Question 10: The heat of formation, ΔH_f° , is equal to 0 for which of the following molecules:

- A H_2O (liquid)
- B Hg (solid)
- C O_2 (gas)
- D CO_2 (gas)

Question 11: For a reversible process:

- A $\Delta S > 0$
- B $\Delta S = 0$
- C $\Delta S < 0$
- D $\Delta S \rightarrow 0$

Question 12: Which of the following occurs in the Daniell cell:



- A Zn(s) is reduced and Cu(aq) is oxidized
- B Cu(aq) is reduced and Zn(s) is oxidized
- C Cu(s) is precipitated and Zn(aq) is dissolved
- D Zn(s) is precipitated and Cu(aq) is dissolved

Question 13: In a reversible adiabatic expansion of an ideal gas:

- A q is not equal to zero
- B w is equal to zero
- C there is a decrease in temperature
- D $\Delta H = 0$

Question 14: Heat never flows spontaneously from low to high temperature because:

- A Then there is an increase in entropy
- B Then there is a decrease in entropy
- C Heat is not a state function
- D The Gibbs energy is increased

Question 15: For a closed, isolated system, the internal energy is:

- A constant
- B minimized
- C maximized
- D an increasing function

Question 16: A process can spontaneously go from state A to state B if the Gibbs energy of the two systems are as follows:

- A $G_A < G_B$
- B $G_A = G_B$
- C $G_A \sim G_B$
- D $G_A > G_B$

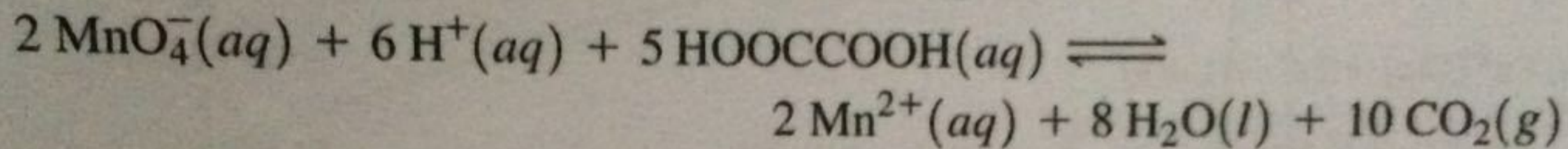
Question 17: In a reversible adiabatic expansion of an ideal gas:

- A $\Delta U = 0$
- B $\Delta H = 0$
- C $q = 0$
- D $\Delta S = 0$

Question 18: In a reversible isothermal expansion of an ideal gas:

- A $w=0$
- B $q=0$
- C $\Delta S=0$
- D $\Delta H=0$

Question 19: The activity coefficient, Q , for the following reaction is:



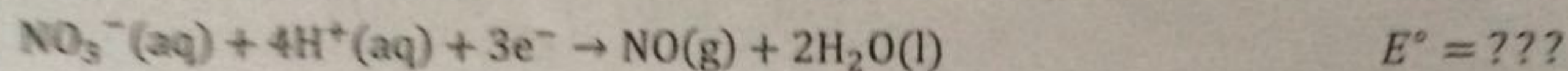
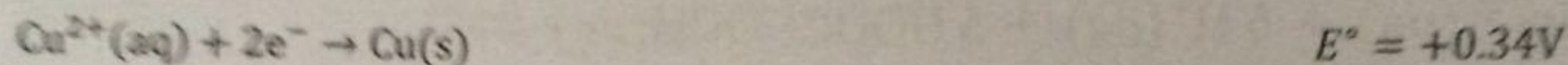
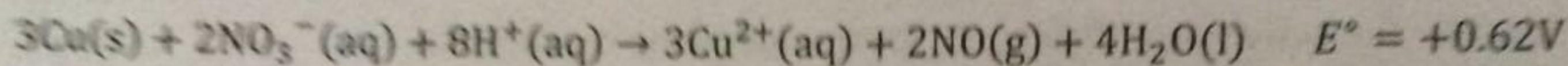
- A $Q = [\text{a}_{\text{H}_2\text{O}}][\text{a}_{\text{CO}_2}] / [\text{a}_{\text{HOOC}(\text{COOH})}]^5$
- B $Q = [\text{a}_{\text{MnO}_4^-}][\text{a}_{\text{H}^+}][\text{a}_{\text{HOOC}(\text{COOH})}] / [\text{a}_{\text{Mn}^{2+}}][\text{a}_{\text{H}_2\text{O}}][\text{a}_{\text{CO}_2}]^x$
- C $Q = [\text{a}_{\text{Mn}^{2+}}][\text{a}_{\text{H}_2\text{O}}][\text{a}_{\text{CO}_2}] / [\text{a}_{\text{MnO}_4^-}][\text{a}_{\text{H}^+}][\text{a}_{\text{HOOC}(\text{COOH})}]$
- D $Q = [2\text{a}_{\text{Mn}^{2+}}][8\text{a}_{\text{H}_2\text{O}}][10\text{a}_{\text{CO}_2}] / [2\text{a}_{\text{MnO}_4^-}][6\text{a}_{\text{H}^+}][5\text{a}_{\text{HOOC}(\text{COOH})}]$

Question 20: For a thermodynamic system that undergoes only PV work, if the pressure is constant:

- A $\Delta V=0$
- B $w=0$
- C $PV=nRT$
- D $\Delta H=q_p$

Question 2: Electrochemistry (30 points)

The reaction between solid copper and nitric acid to form copper (II) ion, nitrogen monoxide gas, and water is represented by the following equation:



- Calculate the standard reduction potential, E° , for the reduction of NO_3^- in acidic solution (5 points).
- Calculate the value of the standard free energy change, ΔG° , for the overall reaction between solid copper and nitric acid (5 points).
- Determine the equilibrium constant, K , for the overall reaction at 298.15 K (5 points).

Experimentally, it is found that the cell potential varies with temperature according to the following equation: $E^\circ = 1.10219 + 42.2 \times 10^{-6} \cdot T + 99.1 \times 10^{-8} \cdot T^2$.

- Calculate the change in the cell potential as the temperature is increased from RT to 72°C (5 points).
Room temperature
- Calculate the reaction entropy, ΔS_R° , for this cell at 72°C (5 points).
- Calculate the reaction enthalpy, ΔH_R° , for this cell at 72°C (5 points).

Question 3: Phase Diagrams (25 points)

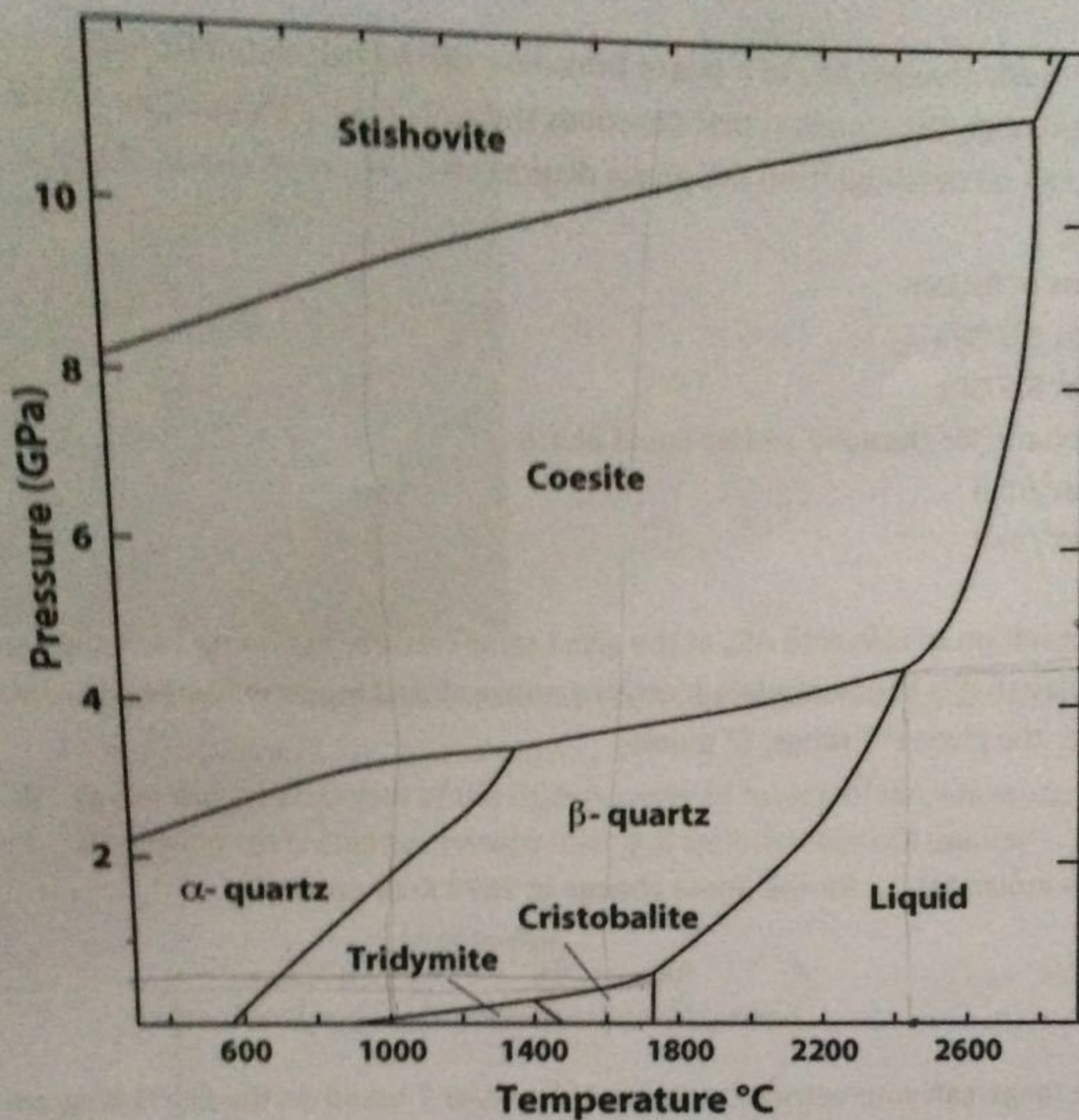


Figure 1: PT phase diagram for the SiO₂ system.

(Source: http://serc.carleton.edu/research_education/equilibria/metamorphic_diagrams.html)

Authors: Dexter Perkins/John Brady based on Swamy&Saxema, 1994)

The phase diagram seen in Figure 1 shows the various phases of silicon dioxide for conditions common in the earth's crust and mantle.

- (a) Examine the phase diagram, and indicate in the table below whether the change in molar volume and molar entropy for the following phase transitions is positive or negative: (4 points)

From-to	ΔS_m	ΔV_m
β-quartz to liquid		
Stishovite to liquid		
Tridymite to cristobalite		
Liquid to coesite		

(b) The molar entropy change, ΔS_m of a phase transition can be calculated from the Clayperon equation, the equation that describes the coexistence curve. The following information can be obtained from the phase diagram for the phase change from coesite to liquid SiO_2 :

Temperatures of fusion:

$$T_1 = 2873 \text{ K at } 6.0 \text{ GPa}$$

$$T_2 = 2923 \text{ K at } 6.5 \text{ GPa}$$

The molar volume for the solid and the liquid phase

$$V_1 = 23.23 \text{ cm}^3/\text{mol}$$

$$V_2 = 21.48 \text{ cm}^3/\text{mol}$$

Use this information to calculate ΔS_m at the given temperature, assuming both the entropy change that is to be calculated, and the above stated molar volumes, are constant over the given P-T range. (7 points)

(c) Calculate the molar ΔH_{fusion} for the phase change at 2873 K: (5 points)

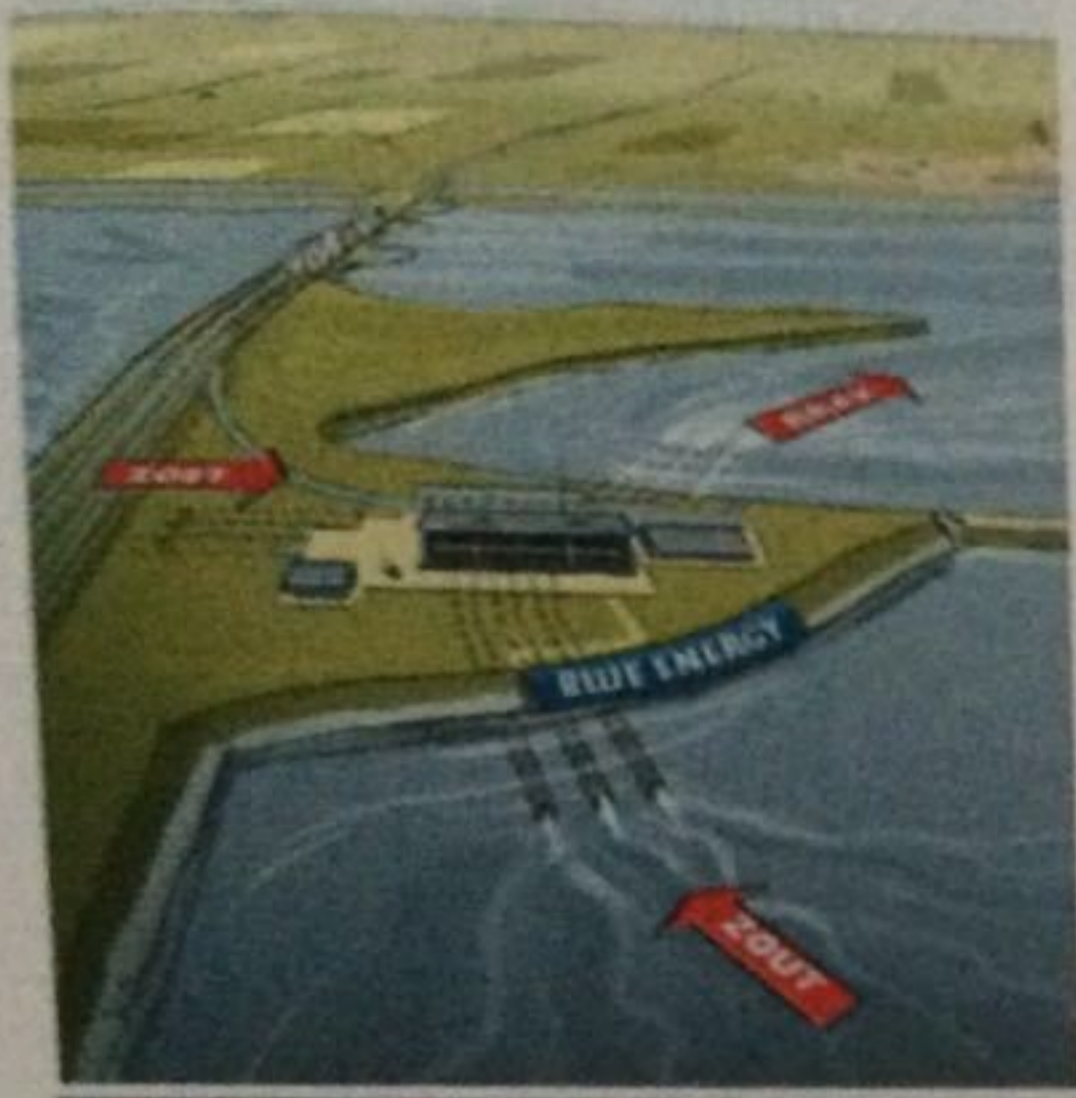
(d) Within what range can you restrict the values of P and/or T based on the phase diagram and the following situations:

1.) The SiO_2 liquid, β -quartz and coesite coexist in equilibrium. (2 points)

2.) As the temperature is increased, β -quartz is first converted into cristobalite and then into liquid. (2 points)

(e) A SiO_2 -bearing rock at a depth of 68 km below the earth's surface has a temperature of 1000K. Through movements in the earth's mantle, the rock travels down to a depth of 340 km, where the temperature turns out to be 1500K. Determine, using an average rock density of 3000 kg/m^3 and the phase diagram in Figure 1, what the stable phases for the SiO_2 are at the initial and final depths. Does the SiO_2 go through any other phases during the transition from initial to final depth? (5 points)

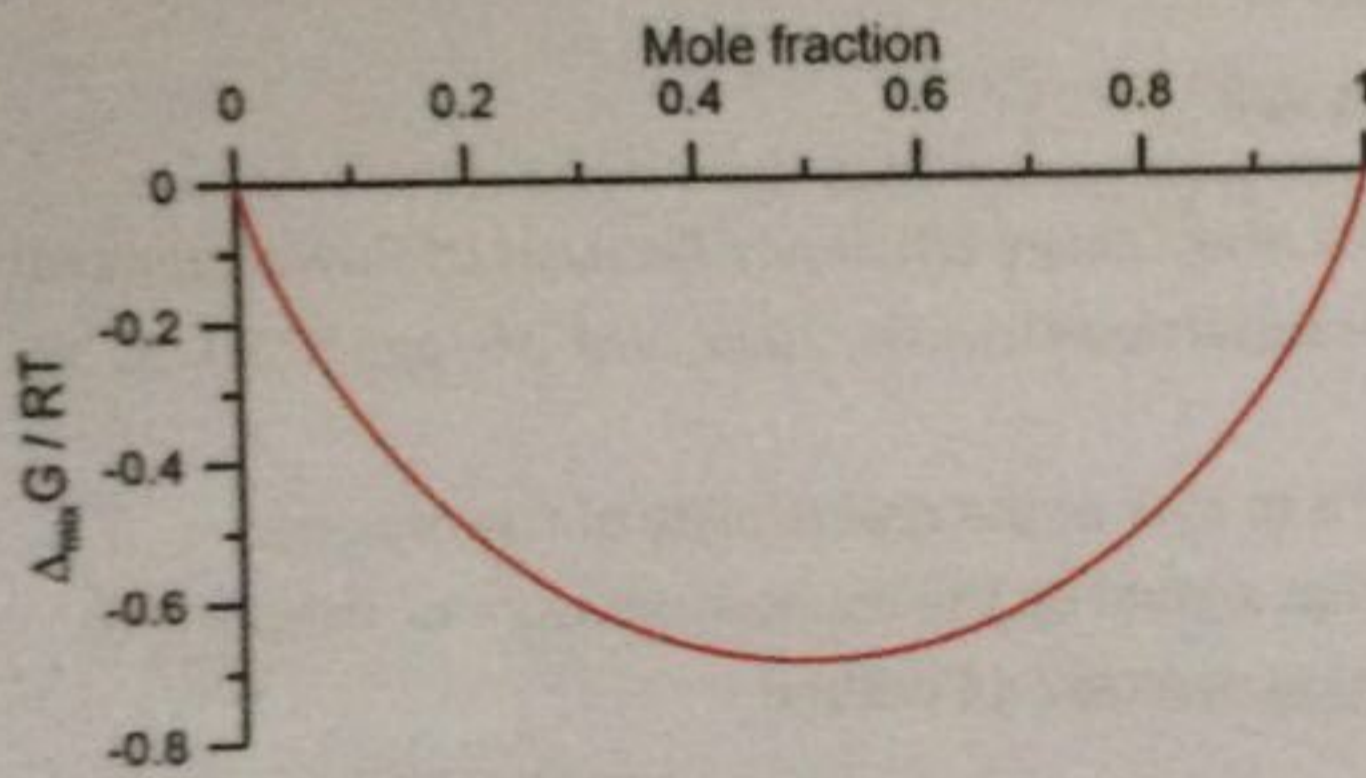
Question 4: Gibbs Energy and 'Blue Energy' (25 points)



From: Rijkswaterstaat

The mixing of fresh water and salt water can be used to gain energy, which is called Blue energy.

- a) Given the graph below of the Gibbs energy of mixing of ideal mixtures can you explain why de-mixing costs energy and why mixing is spontaneous? (3 points)



- b) For 1 liter of seawater in the Dead sea, it is given:

$$n_{Na^+} \approx n_{Cl^-} \approx 5$$

$$n_{water} \approx 55$$

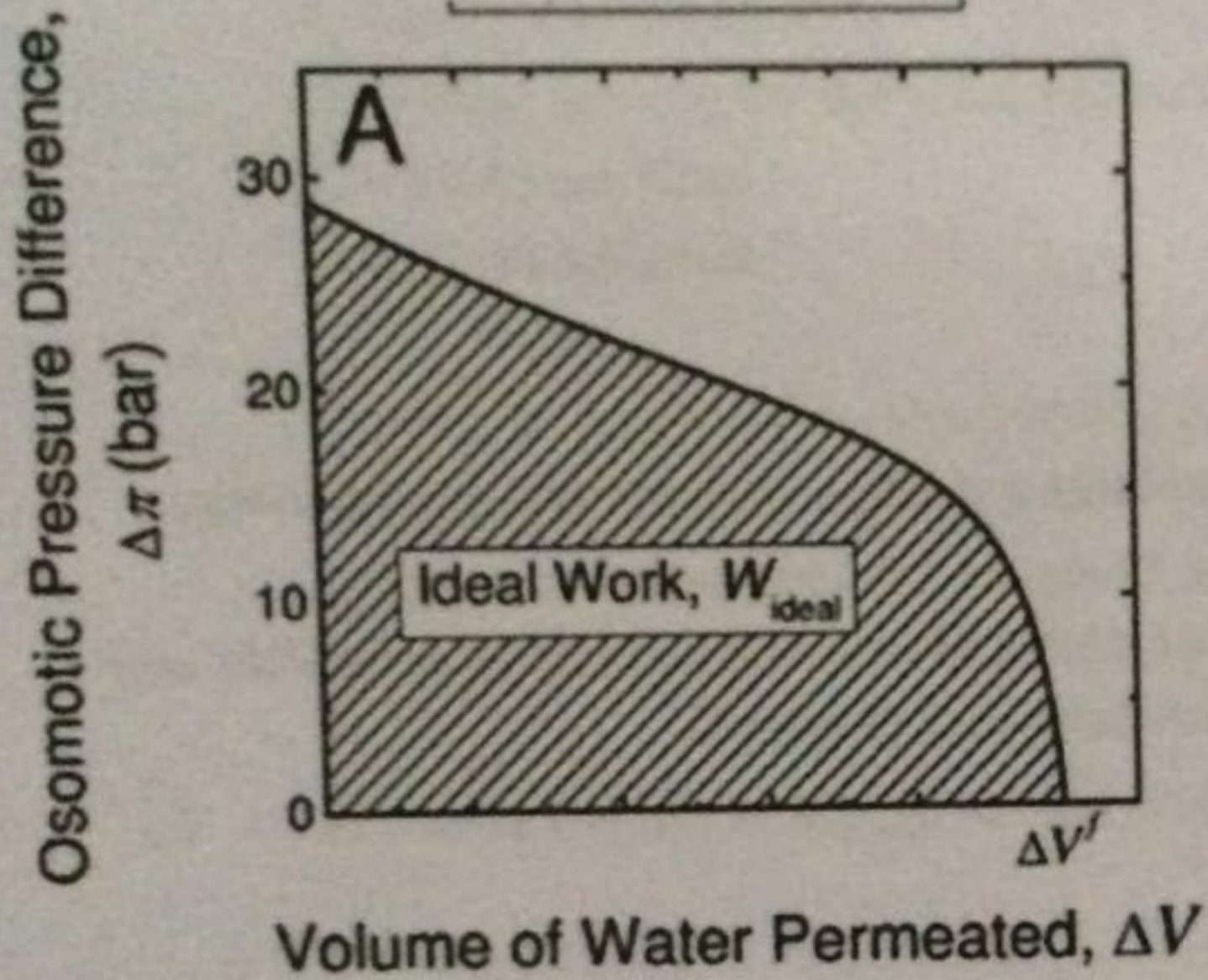
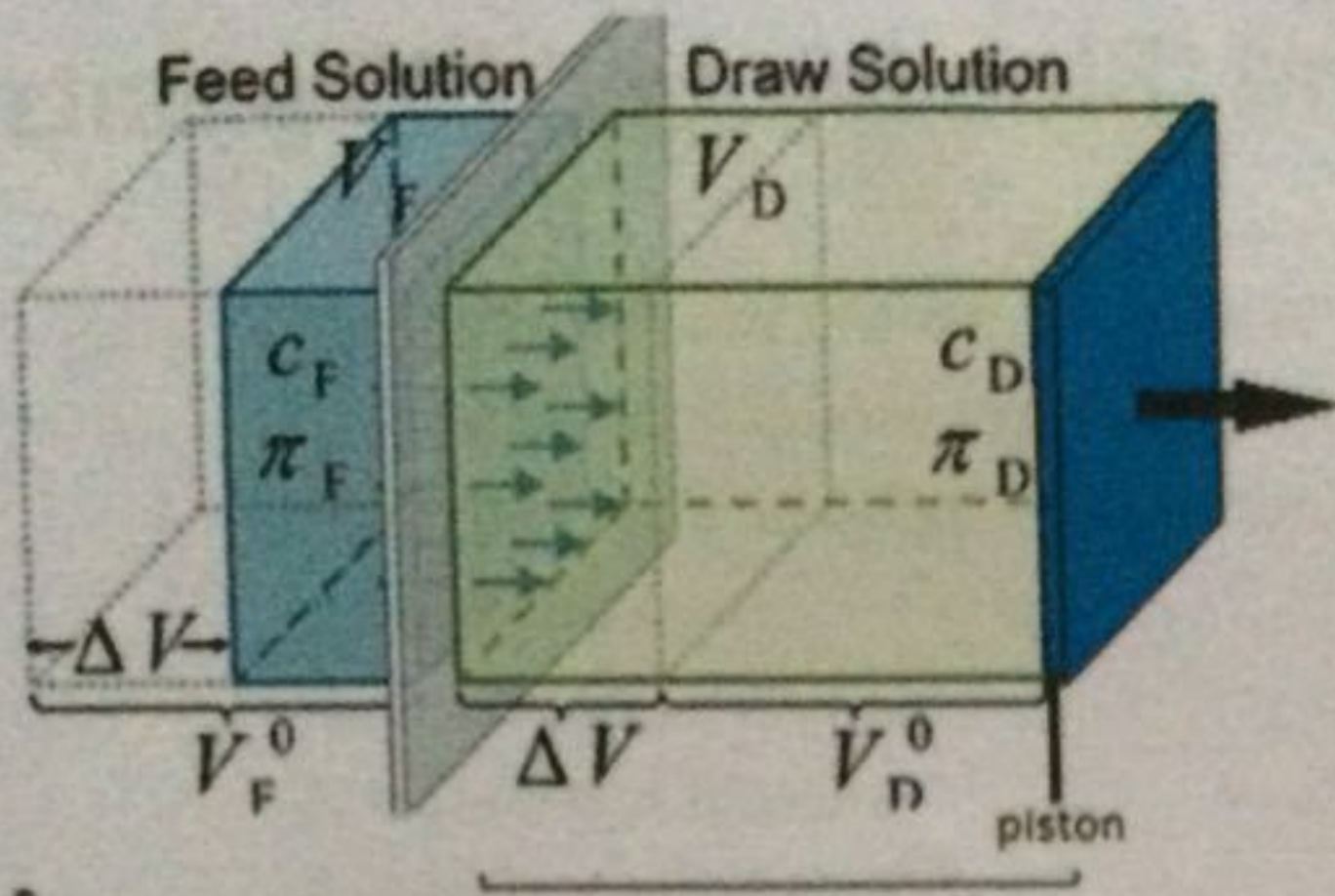
$$T = 300K$$

$$x_{Na^+, seawater} \approx x_{Cl^-, seawater} \approx 0.1$$

$$x_{Na^+, freshwater} \approx x_{Cl^-, freshwater} \approx 0$$

What is the change of Gibbs energy if $1m^3$ of seawater is mixed with $1m^3$ fresh water? (6 points)

- c) The following system shows the process of mixing fresh and salt water. The difference in osmotic pressure causes the salt water to go to the freshwater. The work done on the piston by this system is converted to energy.



(Yip et al, Env. Sci & Techn., Thermodynamic and Energy Efficiency Analysis of Power generation from Natural Salinity Gradients by Pressure Retarded Osmosis, 2012, Vol. 46, pgs 5230~5239)

For the efficiency of this system it is important to look at the reversibility of the process. How can we let this system run reversibly, what should be the counter pressure of the piston? What are the problems when the system runs in reverse? (6 points)

d) Given the following data at $T = 298.15 \text{ K}$:

$$\Delta H_f^\circ \text{ of } \text{H}_2\text{O}(\text{l}) = -285.8 \text{ kJ} \times \text{mol}^{-1}$$

$$\Delta H_f^\circ \text{ of } \text{CO}_2(\text{g}) = -393.5 \text{ kJ} \times \text{mol}^{-1}$$

$$\Delta H_f^\circ \text{ of } \text{CH}_4(\text{g}) = -74.6 \text{ kJ} \times \text{mol}^{-1}$$

Calculate ΔU_R° for the combustion of methane. (6 points)

e) Looking at the two ways to gain energy (blue energy and combustion of methane) what can be said about the difference of the change of enthalpy and therefore the difference in energy density? You may assume that the mixtures are ideal. (4 points)