

ANSWER ONLY SIX QUESTIONS OUT OF SEVEN AND INDICATE WHICH QUESTIONS YOU HAVE ANSWERED BY CIRCLING THE CORRESPONDING NUMBERS ON THE FRONT OF YOUR FIRST EXAMINATION BOOKLET.

Each question will have equal weight. Start each question at the top of a new page.

No aids are permitted. Any non-programmable calculator may be used.

Given Information

$$R = 8.314 \text{ J/(mol K)} \quad 1 \text{ F} = 96,487 \text{ J/(V mol)} \quad 1 \text{ atm} = 101.325 \text{ kPa} = 760 \text{ mmHg}$$

molar masses (g/mol) C: 12.0, H: 1.01, O: 16.0

$$\ln \left[ \frac{P_{\text{vap}1}}{P_{\text{vap}2}} \right] = -\frac{\Delta H_{\text{vap}}}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] \quad E = E^0 - \frac{RT}{nF} \ln Q$$

$$\text{At } 25^\circ\text{C} \quad E = E^0 - \frac{0.0591}{n} \log Q$$

$$TdS = C_p dT - T(\partial V/\partial T)_p dp \quad TdS = C_v dy + T(\partial^2 \ln T/\partial y^2) dy$$

i) a) For the reaction  $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$ , determine  $\Delta G_{\text{rxn}}^0$  under standard conditions.

b) What is the equilibrium partial pressure of  $\text{CO}_2$  at  $25^\circ\text{C}$ ?

c) What is the lowest temperature at which  $\text{CaO}$  could be formed if the partial pressure of  $\text{CO}_2$  is one atmosphere? State any assumptions needed to do this calculation.

Species	$\Delta H_f^0$ (at $25^\circ\text{C}$ )	$\Delta S_f^0$ (at $25^\circ\text{C}$ )
$\text{CaCO}_3$	-1206.9 kJ/mol	92.9 J/(mol K)
$\text{CaO}$	-635.1 kJ/mol	39.8 J/(mol K)
$\text{CO}_2$	-393.5 kJ/mol	213.6 J/(mol K)

2) 3.00 moles of gas consisting of benzene ( $\text{C}_6\text{H}_6$ ), propane ( $\text{C}_3\text{H}_8$ ) and ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) were combined with 24.0 moles of oxygen in a 100.0 liter constant volume reactor. The mixture was burned completely to  $\text{CO}_2$  and to  $\text{H}_2\text{O}$  vapour. After combustion there were a total of 29.4 moles of gas. It was known that the number of moles of ethanol and propane was the same at the start of the reaction.

a) What was the mole ratio of benzene to ethanol at the start of the reaction?

b) If after the combustion the reactor was at  $100^\circ\text{C}$ , what was the partial pressure of the oxygen that was remaining?

c) What was the mole fraction of oxygen after the reaction?

3) a) Calculate the vapour pressure of an ideal solution of 100.0g of glucose (mm = 180.2g/mol) in 1.000 kg of water at  $100.0^\circ\text{C}$ .

b) What would the temperature have to be for the partial pressure of water in equilibrium with this solution to be 1.000 atm? (Use  $0^\circ\text{C} = 273.15\text{K}$  for this question;  $\Delta H_v^0(\text{H}_2\text{O}) = 40.79 \text{ kJ/mol}$  at  $100^\circ\text{C}$ )

c) Using your answer from part b), calculate the molal boiling point elevation constant,  $K_b$ , for water.

4) a) A tank being used to store ethylene gas ( $\text{C}_2\text{H}_4$ ) is to be filled using a scale. The tank has a volume of 10.0L, and it is capable of sustaining an internal pressure of 75.0 atm. Calculate the mass of ethylene which can be safely stored in the tank at  $25.0^\circ\text{C}$  using

- the ideal gas law, and  $\gamma$
- the generalized compressibility chart attached.  $\gamma$

Data: For ethylene:  $T_c = 283\text{K}$  and  $P_c = 50.5 \text{ atm}$ .

b) Explain, using a sketch of a P versus V diagram (with contours of constant T), why the contour for Z versus  $P_r$  on the generalized compressibility chart has an infinite slope at  $P_r = T_r = 1.0$ . You may wish to make use of the fact that  $(\partial x/\partial y)_w = (\partial x/\partial y)_w$ .

5) a) Calculate  $\Delta S$  for the process



b) Show that entropy is a state function by calculating  $\Delta S$  for the same process using a different path. List any assumptions needed to do this calculation.

Data:  $C_p(\text{H}_2\text{O}(l)) = 75.3 \text{ J/(mol K)}$ ;  $C_p(\text{H}_2\text{O}(g)) = 33.6 \text{ J/(mol K)}$

$$\Delta H_v^\circ(\text{H}_2\text{O}) = 40.79 \text{ kJ/mol at } 100^\circ\text{C}$$

$$\Delta S = C_p \ln \frac{T_2}{T_1} + \frac{\Delta H_v}{T_2}$$

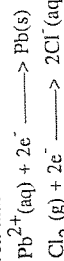
6. (a) Joe Skule was studying the kinetics of the reaction



by taking 5 moles of A and reacting these with 15 moles of B. He found that after 5.00 minutes half of the reactant A had disappeared. From this observation, calculate the rate constant for the reaction if

- The reaction is first order; i.e.,  $d[A]/dt = -k_1[A]$
- The reaction is second order; i.e.,  $d[A]/dt = -k_2[A][B]$

(b) Given that



$$E^\circ = -0.13 \text{ V}$$

$$E^\circ = 1.36 \text{ V}$$

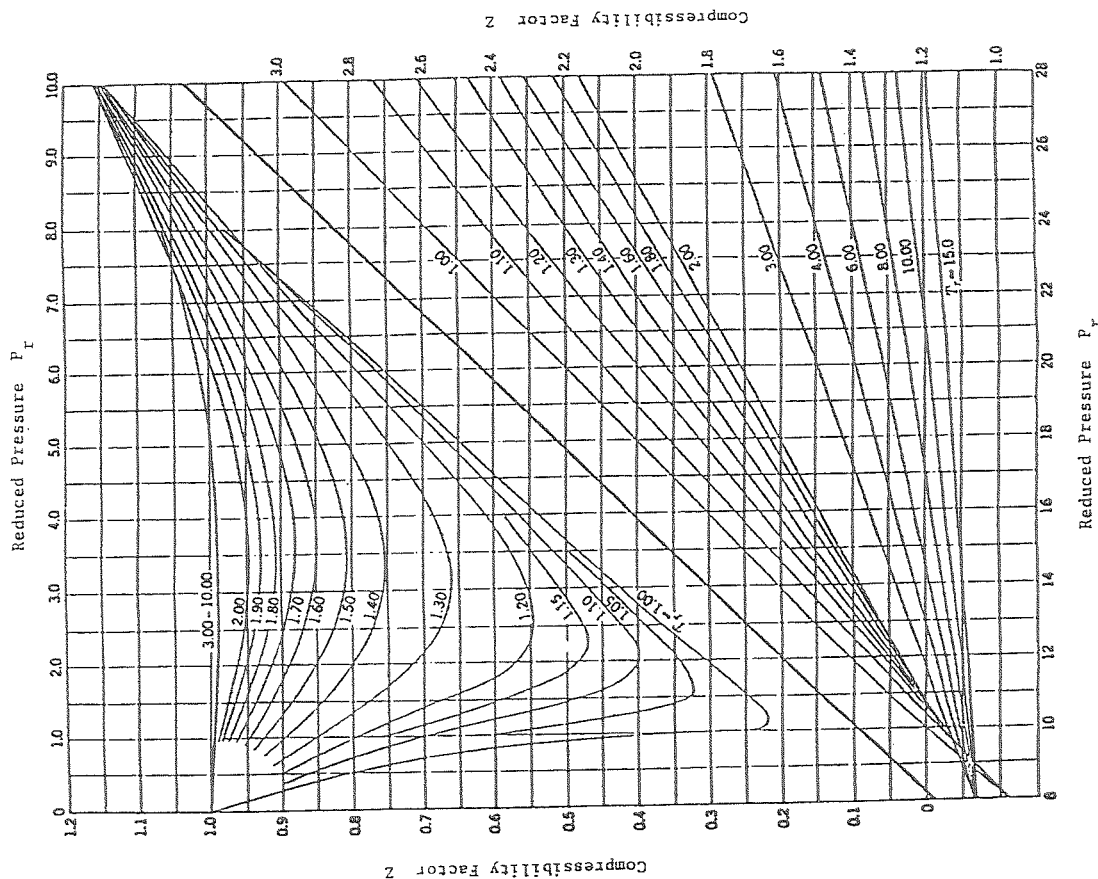
determine the solubility product of lead chloride under standard conditions.

$$M_{\text{sol}} \text{ give } \Delta G_v \neq \Delta G_{\text{Cl}_2}$$

7. (a) 2.00 moles of air are compressed very rapidly and adiabatically from 1.00 atm and 298 K to 50.0 atm. Derive an expression for the temperature rise and calculate the temperature of the compressed air, given that for air the ratio of heat capacities  $\gamma = C_p/C_v$  is 1.402. State clearly any assumptions that you make.

(b) 2.00 moles of air are compressed isothermally from 1.00 atm, 298 K to 50.0 atm. Calculate the change in entropy of the air.

(c) If in (a) after compression the air is allowed to cool to 298 K, calculate the change in entropy of the air? How does your answer here compare to (b)? Which process yields greater entropy change of the air, and why?



\* J.M. Smith and H.C. Van Ness, Introduction to Chemical Engineering Thermodynamics, McGraw-Hill, (1959).