

Answer three of the following four multiple choice questions for 15 points each:

1. How many degrees of freedom are present in an alloy of copper and zinc (only a single homogenous solid phase).

A) 0 B) 1 C) 2 D) 3 E) 4

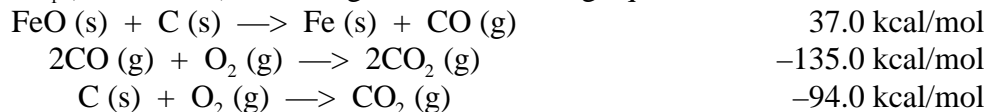
Since $c = 2$, $p = 1$, from the phase rule $f = c - p + 2 = 2 - 1 + 2 = 3$ (T, p, x_{Cu}). Thus answer D is correct.

2. What is the equilibrium constant (K_p) for the reaction $N_2 + O_2 \rightleftharpoons 2 NO$ given the free energy of formation of NO, $G_f^\circ = 86.55$ kJ/mol?

A) 4.56×10^{-31} B) 6.75×10^{-16} C) 86.55 D) 1.48×10^{15} E) 2.19×10^{30}

Using the equation $\Delta G^\circ = -RT \ln K_p$, we solve for $K_p = \exp(-\Delta G^\circ / RT)$. For this reaction, $\Delta G^\circ = 2 \Delta G_{f,NO}^\circ - \Delta G_{f,O_2}^\circ - \Delta G_{f,N_2}^\circ = 173.1$ kJ/mol. Putting this into the equation for $K_p = \exp(-173100 / 8.31451 / 298) = 4.56 \times 10^{-31}$ (answer A).

3. Calculate the H_f (in kcal/mol) for FeO given the following equations:



A) -192.0 B) -127.0 C) -63.5 D) -33.0 E) +33.0

We reverse reaction 1, reverse reaction 2 and divide by 2 (to balance CO) and add reaction 3 (to balance CO₂). Net reaction is formation of FeO and has $\Delta H_f = -63.5$ kcal/mol (answer C).

4. What is the entropy change when 180.2 g (10.00 mol) of liquid water is pressurized from 1.00 atm to 21.00 atm at 298 K. For water, assume $\alpha = 3.04 \times 10^{-4} \text{ K}^{-1}$ and $\beta = 1.00 \text{ g/cm}^3$ over the entire pressure range of this problem.

A) -0.111 J / K B) -0.00337 J / K C) 0.00 J / K D) 0.00337 J / K E) 0.111 J / K

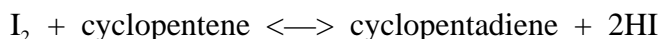
Using the equation that $dS = -\alpha V dP$ and integrating this gives: $\Delta S = -\alpha V \Delta P$ (assuming α and V are constants over pressure range). $\Delta S = -(0.000304 \text{ K}^{-1})(180.2 \text{ g})(1.00 \text{ cm}^3 / \text{g})(20 \text{ atm}) [(8.31451 \text{ J/mol K}) / (82.06 \text{ atm cm}^3 / \text{mol K})] = -0.111 \text{ J/K}$.

Choose three of the following four problems for 35 points each:

5. Calculate G for the isothermal compression of 30.0 g of water from 1.0 atm to 100.0 atm at 25°C; neglect the variation of V with P .

Using the equation $dG = V dP$ and integrating this gives $\Delta G = V \Delta P = (30.0 \text{ cm}^3)(99 \text{ atm}) [(8.31451 \text{ J/mol K}) / (82.056 \text{ cm}^3 \text{ atm/mol K})] = 300.9 \text{ J}$.

6. For the gas-phase reaction



measured K_p° values in the range of 450 to 700K are fitted by:

$$\ln K_p^\circ = a + b/T$$

where $a = 7.55$ and $b = -4.83 \times 10^3 \text{ K}$. Calculate G° , H° , and S° for this reaction at 500K. Assume ideal gases.

Using $\Delta G^\circ = -RT \ln K_p^\circ = -(8.31451 \text{ J/mol K})(500 \text{ K})(7.55 - (4830/500)) = +8771 \text{ J/mol}$.

For ΔH° and ΔS° we need to use $\ln K_p^\circ = -\Delta H^\circ/RT + \Delta S^\circ/R$. Thus $a = \Delta S^\circ/R$ giving $\Delta S^\circ = 7.55(8.31451 \text{ J/mol K}) = 62.77 \text{ J/mol K}$ and $b = -\Delta H^\circ/R$ gives $\Delta H^\circ = 4830 \text{ K}(8.31451 \text{ J/mol K}) = 40,159 \text{ J/mol}$.

7. The normal melting point of Ni is 1452°C. The vapor pressure of liquid Ni is 0.100 torr at 1606°C and 1.00 torr at 1805°C. The molar heat of fusion of Ni is 4.2 kcal/mol. Making reasonable approximations, estimate the triple point and vapor pressure of solid Ni at 1200 °C.

The first step is determining the triple point. The liquid/solid slope will be nearly infinite so the triple point temperature will be basically identical to the normal melting point (1452 °C). The heat of vaporization is determined using the Clapeyron equation applied to the liquid/vapor transition (the two other data points given in the problem). Integrating this equation gives

$$\begin{aligned} \ln(P_2/P_1) &= \ln(1 \text{ torr}/0.1 \text{ torr}) = -(\Delta H/R)(1/T_2 - 1/T_1) \\ 2.302 &= -(\Delta H/(8.31451 \text{ J/mol K}))(1/2078\text{K} - 1/1879\text{K}) \\ \Delta H_{\text{vap}} &= 375544 \text{ J/mol} \end{aligned}$$

Using this enthalpy, we may calculate the pressure at the triple point using the same equation:

$$\begin{aligned} \ln(p_2/0.1 \text{ torr}) &= -(375544 \text{ J/mol}/(8.31451 \text{ J/mol K}))(1/1725\text{K} - 1/1879\text{K}) \\ p_2 &= 0.011 \text{ torr} \end{aligned}$$

From this point we need to extrapolate back to 1200 °C using the Clapeyron equation, $d \ln P / dT = \Delta H / RT^2$. We need to know the ΔH_{sub} , which is essentially the $\Delta H_{\text{vap}} + \Delta H_{\text{fus}}$. This yields a value of $\Delta H_{\text{sub}} = 375544 \text{ J/mol} + [4200 \text{ cal/mol}(4.184 \text{ J/cal})] = 393117 \text{ J/mol}$. Lastly, using the Clapeyron equation you may back calculate the vapor pressure from the triple point (1452°C & 0.011 torr).

$$\begin{aligned} \ln(p_2/0.011 \text{ torr}) &= -(393117 \text{ J/mol}/(8.31451 \text{ J/mol K}))(1/1473\text{K} - 1/1725\text{K}) \\ p_2 &= 0.000101 \text{ torr} \end{aligned}$$

8. For $\text{CH}_3\text{OH}(\text{l})$ at 25°C, the vapor pressure is 125 torr, H_m of vaporization is 37.9 kJ/mol, H_f is -238.7 kJ/mol, and S_m° is 126.8 J/mol K. Making reasonable approximations, find H_f° and S_m° of $\text{CH}_3\text{OH}(\text{g})$.

To get the ΔH_f° of $\text{CH}_3\text{OH}(\text{g})$ we need to determine the enthalpy of the vaporization at 1 bar and 25°C. This should be basically the same as the enthalpy of vaporization at the normal boiling point or 37.9 kJ/mol (since ΔH° is relatively temperature independent, assuming the heat capacities of liquid and gas are similar). The ΔH_f° will be $-238.7 + 37.9 \text{ kJ/mol} = -200.8 \text{ kJ/mol}$. To determine the S_m° we need the normal boiling point temperature. From the Clapeyron equation:

$$\begin{aligned} \ln(P_2/P_1) &= \ln(750 \text{ torr}/125 \text{ torr}) = -(\Delta H/R)(1/T_2 - 1/T_1) \\ 1.792 &= -(37900/(8.31451 \text{ J/mol K}))(1/T_2 - 1/298\text{K}) \\ T_2 &= 337.5 \text{ K} = 64.5^\circ\text{C} \end{aligned}$$

The $\Delta S_{\text{vap}}^\circ = (37900 \text{ J/mol})/(337.5 \text{ K}) = 112.3 \text{ J/mol K}$. Again, assuming that ΔS° due to the temperature difference is negligible (good approximation if the heat capacities of the liquid and gas are similar) then $S_m^\circ = 126.8 + 112.3 \text{ J/mol K} = 239.1 \text{ J/mol K}$.