**1.** a volume of 1.0 L to 10.1 L

Against an external pressure of 0.50 atm

The gas absorbs 250 J of heat from the surroundings

q, w and  $\Delta U (\Delta E) = ?$ 

$$\mathbf{q}$$
= +250 j  
 $\mathbf{w}$ = - P ×  $\Delta$ V= -(0.50 atm) × (10.1 L – 1.0 L)= -4.55 atm × (101.3 J/1 L.atm)= -460.915 J  
 $\Delta$ E=  $\Delta$ U=  $\mathbf{q}$  +  $\mathbf{w}$  = +250 J + (-460.915 J)= -210.915 J

**2.**  $\Delta H^{o}_{ol}[HCl_{(g)}] = -92.31 \text{ kJ}$ 

$$\Delta H^{o}_{ol}[CH_{4(g)}] = -74.81 \text{ kJ}$$

$$CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(g) + 4 HCl(s)$$
  $\Delta H^0 = -397.3 \text{ kJ}$ 

The standard enthalpy of formation of CCl<sub>4</sub>(g) at 25 °C and 1 bar.

$$\begin{split} \Delta H^o{}_{rxn} &= \left[\Delta H^o{}_{ol}(CCl_4(g) + 4\Delta H^o{}_{ol}(HCl_{(g)})\right] - \left[\Delta H^o{}_{ol}(CH_{4(g)}) + 4\Delta H^o{}_{ol}(Cl_{2(g)})\right] \\ -397.3 \text{ kJ} &= \left[\Delta H^o{}_{ol}(CCl_4(g) + 4\times -92.31 \text{ kJ}\right] - \left[-74.81 \text{ kJ} + 4\times 0 \text{ kJ}\right] \\ \Delta H^o{}_{ol}(CCl_4(g)) &= -102.87 \text{ kJ} \end{split}$$

**3.** 50 g of iron that has an initial temperature of 225 °C and 50 g of gold that has an initial temperature of 25 °C

no heat is lost to the surroundings, what will be the temperature when the two metals reach **thermal equilibrium?** 

The specific heat capacity of iron: 0.449 J/g°C and gold: 0.128 J/g°C

$$\begin{split} q_{Au} + q_{Fe} &= 0 \\ q_{Au} &= \text{-} \ q_{Fe} \\ q_{Au} &= m_{Au} \times S_{Au} \times \Delta t = 50g \times 0.128 \ \text{J/g°C} \times (t_{f}\text{-}25 \ ^{\circ}\text{C}) \\ q_{Fe} &= m_{Fe} \times S_{Fe} \times \Delta t = 50g \times 0.449 \ \text{J/g°C} \times (t_{f}\text{-}225 \ ^{\circ}\text{C}) \\ q_{Au} &= \text{-} \ q_{Fe} \\ 50g \times 0.128 \ \text{J/g°C} \times (t_{f}\text{-}25 \ ^{\circ}\text{C}) &= \text{-} \ (50g \times 0.449 \ \text{J/g°C} \times (t_{f}\text{-}225 \ ^{\circ}\text{C})) \\ t_{f} &= 180.55 \ ^{\circ}\text{C} \end{split}$$

**4. increasing boiling point**: CH<sub>3</sub>CH<sub>2</sub>OH, HOCH<sub>2</sub>CH<sub>2</sub>OH, CH<sub>3</sub>CH<sub>2</sub>Cl, and ClCH<sub>2</sub>CH<sub>2</sub>OH

CH<sub>3</sub>CH<sub>2</sub>Cl< CH<sub>3</sub>CH<sub>2</sub>OH< ClCH<sub>2</sub>CH<sub>2</sub>OH< HOCH<sub>2</sub>CH<sub>2</sub>OH

5. increasing boiling point and vapor pressure: CH<sub>3</sub>OH, He, CH<sub>3</sub>Cl and N<sub>2</sub>

**Boiling point:** He< N<sub>2</sub>< CH<sub>3</sub>Cl< CH<sub>3</sub>OH **Vapor pressure:** He>N<sub>2</sub>> CH<sub>3</sub>Cl> CH<sub>3</sub>OH

**6.** Europium crystallizes in a body-centered cubic lattice

The density of Eu is 5.26 g/cm<sup>3</sup>

Calculate the unit cell edge length in pm. (Eu MW:152 g/mol).

m= (2 Eu atoms/1 unit cell) × (1 mol Eu/6.022 ×  $10^{23}$  Eu atoms) × (152.0 g Eu/1mol Eu) = 5.048 ×  $10^{-22}$  g Eu/unit cell V= (5.048 ×  $10^{-22}$  g Eu/1 unit cell) × (1 cm<sup>3</sup>/5.26g)= 9.60 ×  $10^{-23}$  cm<sup>3</sup>/unit cell a=  $V^{1/3}$ = (9.60 ×  $10^{-23}$  cm<sup>3</sup>)  $^{1/3}$ = 4.58 ×  $10^{-8}$  cm=458 pm

**7.** The density of an aqueous solution containing 10.0 percent of C<sub>2</sub>H<sub>5</sub>OH by mass is 0.984 g/mL.

Molality, molarity, what volume of the solution would contain 0.125 mole of ethanol?  $(M_C=12.01, M_H=1.008, M_O=16.00)$ 

```
Assume 100 g of solution
0.1 × 100 g= 10g ethanol
100g-10g= 90g=0.090 kg water

10 g ethanol × (1mol/46.07g)= 0.217 mol ethanol
m= mol solute/kg solvent= 0.217mol/0.090kg= 2.41m

100g × (1mL/0.984g)= 102 mL= 0.102 L
M=(mol solute/liters of soln)=0.217mol/0.102L= 2.13 M

0.125mol × (1L/2.13mol)= 0.0587L= 58.7mL
```

**8.** 0.100 g of lysozyme is dissolved in 150 g of water at 25 °C.

Calculate the vapor-pressure lowering, the depression in freezing point, the elevation in boiling point, and the osmotic pressure of this solution.

**Molar mass of lysozyme** = 13930 g/mol

Molar mass of water = 18.02 g/mol

**density of the solution** = 1 g/mL

 $P_{water}^0 = 23.76 \text{ mmHg at } 25 \,^{\circ}\text{C}$ 

 $K_f = 1.86 \, {}^{\circ}\text{C/m}$ 

 $K_b = 0.52 \, {}^{\circ}\text{C/m}$ 

R = 0.0821 L.atm/mol.K

```
\begin{array}{l} n_{lysozyme} \!\!=\!\! 0.10g \times (1mol/13930g) \!\!=\! 7.18 \times 10^{\text{-}6} mol \\ n_{water} \!\!=\! 150g \times (1mol/18.02g) \!\!=\! 8.32 \; mol \end{array}
```

## **Vapor-pressure lowering:**

$$\begin{split} \Delta P &= X_{lysozyme} \times P^{\circ}_{water} = (n_{lysozyme}/(n_{lysozyme} + n_{water})) \times (23.76 \text{ mmHg}) \\ &= (7.18 \times 10^{-6} \text{mol}/(7.18 \times 10^{-6} \text{mol} + 8.32 \text{ mol})) \times (23.76 \text{ mmHg}) = 2.05 \times 10^{-5} \text{ mmHg} \end{split}$$

### Freezing point depression:

$$\Delta T_f = K_f \times m = 1.86 \text{ °C/m} \times (7.18 \times 10^{-6} \text{mol/0.150kg}) = 8.90 \times 10^{-5} \text{ °C}$$

# **Boling point elevation:**

$$\Delta T_b = K_b \times m = 0.52 \text{ °C/m} \times (7.18 \times 10^{-6} \text{mol/} 0.150 \text{kg}) = 2.5 \times 10^{-5} \text{ °C}$$

#### **Osmotic pressure:**

$$\pi$$
=M × R × T= (7.18 × 10<sup>-6</sup>mol/0.150L) × 0.0821 L.atm/mol.K × (298K) = 1.17 × 10<sup>-3</sup> atm=0.889 mmHg

**9.** increasing solubility in water: O<sub>2</sub>, LiCl, Br<sub>2</sub>, (CH<sub>3</sub>OH)

O<sub>2</sub>< Br<sub>2</sub>< LiCl< CH<sub>3</sub>OH

## 10. $A + B \rightarrow products$

### determine the order of the reaction and calculate the rate constant

	[A] (M)	[B] (M)	Rate (M/s)
1	1.50	1.50	$3.20 \times 10^{-1}$
2	1.50	2.50	3.20 x 10 <sup>-1</sup>
3	3.00	1.50	6.40 x 10 <sup>-1</sup>

Compare with first and second sets: Changing [B] does not affect the rate of the reaction, zero order in B

Compare with first and third sets: doubling [A] doubles the rate of the reaction, first order in A

Rate= 
$$k \times [A]$$
  
3.20 x  $10^{-1}$  M/s=  $k \times (1.50 \text{ M})$   
 $k=0.212 \text{ s}^{-1}$ 

$$Rate_{2}/Rate_{1} = (3.20 \text{ x } 10^{-1}/3.20 \text{ x } 10^{-1}) = 1 = (k \times (1.50)^{x} \times (2.50)^{y}) / (k \times (1.50)^{x} \times (1.50)^{y})$$
 y= 0 Zero order for B

Rate<sub>3</sub>/Rate<sub>1</sub>= 
$$(6.40 \times 10^{-1}/3.20 \times 10^{-1})$$
=  $2 = (k \times (3.00)^x \times (1.50)^y)/(k \times (1.50)^x \times (1.50)^y)$   
X= 1 First order for A

11. The rate constant for the second-order reaction is 0.80/M. s at  $10^{\circ}$ C.

Starting with a concentration of 0.086~M, calculate the concentration of NOBr after 22 s. Calculate the half-life when [NOBr]<sub>0</sub>= 0.072~M.

$$2NOBr(g) \rightarrow 2NO(g) + Br_2(g)$$

$$\begin{split} 1/[NOBr]_{t} &= kt + 1/[NOBr]_{0} \\ 1/[NOBr]_{t} &= (0.80/M.s) \ (22s) + 1/0.086M \\ 1/[NOBr]_{t} &= 29 \ M^{\text{-}1} \\ [NOBr]_{t} &= 0.034M \end{split}$$

$$t_{1/2}$$
= 1/k[A]<sub>0</sub>= 1/(0.80/M.s) (0.072M)  
 $t_{1/2}$ = 17 s

**12.** The rate constants of some reactions double with every 10-degree rise in temperature. Assume that a reaction takes place at 295 K and 305 K.

What must the activation energy?

$$\begin{split} &In(k_1/2k_1)\!=E_a/R\times((T_1\text{-}T_2)/\ T_1.T_2)\\ -&0.693\!=E_a/8.314\ J/K.mol\ ((295K\text{-}305K)/295K.305K)\\ &E_a\!=5.18\times10^4\ J/mol\!=51.8\ kJ/mol \end{split}$$