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Find the  $S_{\text{sur}}$  (the surrounding ) and  $S_{\text{univ}}$  (the universe) if 2.000mol of super cooled liquid water at  $-15.00$  freezes irreversibly at constant pressure of 1.000atm ice at –15.00 . Assume the molar heat capacity of liquid water to be constant and equal to  $76.1$ JK $^{-1}$ mol $^{-1}$ ,and that of ice to be constant and equal to  $37.15$ JK<sup>-1</sup>mol<sup>-1</sup>, and the surrounding remain at equilibrium at  $-15.00$ . The latent heat of fusion of water is  $333.5 \text{ Jg}^{-1}$ . (15%)

The Half-life of 235U is equal to  $7.1x10^8$  years (10%)

- a. Find the rate constant.
- b. Find the time required to a sample of 235U to decay to 10.0% of its original amount.

三 (a) Calculate the work done on a closed system consisting of 50.00 g of argon, assumed ideal, when it expands reversibly from a volume of 5.000 L to a volume of 10.00 L at a constant temperature of 298.15 K.  $(5\%)$ 

(b) A system consisting of 2.00 mole of argon, assumed ideal with Cv equal to 3nR/2, expands adiabatically and reversibly from a volume of 5.00 L and a temperature of 373.15 K to a volume of 20.00 L. Find the final temperature and the work. (8%)

四 (a) Write the cell symbol, the cell reaction equation, and the Nernst equation for the cell with the half-reactions

> $2Hg_{(1)} + 2Cl^ Hg_2Cl_{2 (s)} + 2e^ Cl_{2(g)} + 2e^-$  2Cl

(b) Find the potential difference of the cell at 298.15 K if  $P (Cl<sub>2</sub>) = 0.950$  atm and  $a(Cl) = 0.500$ ,  $E^0 = 1.091$  V. (10%)

Find the boiling elevation constant for water and the boiling temperature at 1.00 atm of a solution of sucrose with 10.00 g of sucrose in 1.000kg of water. The molar enthalpy change of vaporization is 40.67KJmol<sup>-1</sup> (sucrose,C12H22O11, 342.3 g/mol). (12%)

Use the cycle rule to show the this equation  $\left| \frac{\partial H}{\partial \mathbf{p}} \right| = -C_p \mu_{J,T}$ . ,  $P$  $\mu$ *J.T T n C*  $\left(\frac{\partial H}{\partial P}\right)_{T,n} = -C_P\mu_p$  $\setminus$ ſ ∂  $\left(\frac{\partial H}{\partial r}\right) = -C_p \mu_{LT}$ , where  $J.T.$   $\left(\frac{\partial P}{\partial P}\right)_{H,n}$ *T* ,  $T_{\rm c} = \frac{\sigma}{2R}$  $\bigg)$  $\left(\frac{\partial T}{\partial \Sigma}\right)$  $\setminus$ ſ ∂  $\mu_{LT} = \left(\frac{\partial T}{\partial \rho}\right)$  is the Joule-Thomson coefficient.(12%) (a) Show that  $\left|\frac{\partial v}{\partial x}\right| = 0$  $\left(\frac{\partial U}{\partial V}\right)_{_{T,n}} =$  $\setminus$ ſ ∂ ∂  $V$   $\big|_{T,n}$  $\begin{pmatrix} U \\ \vdots \end{pmatrix}$  = 0 for an ideal gas, using only the thermodynamic equation of state and *PV* = *nRT*

(b) Find an expression for  $\left(\frac{\partial U}{\partial V}\right)_{T,n}$ ,  $\overline{\phantom{a}}$ J  $\left(\frac{\partial U}{\partial x}\right)$  $\setminus$ ſ ∂  $\left(\frac{\partial U}{\partial \mathbf{r}^2}\right)$  for a gas obeying the van der Waals equation. (13%)

八 Show that the following scheme proposed by R. Ogg, *J. Chem. Phys.,* **15,** 337(1947) is consistent with, and can explain, the observed first-order decomposition of  $N_2O_5$  (15%)

$$
N_2O_5 \underset{k_2}{\Leftrightarrow} NO_2 + NO_3 \tag{1}
$$

$$
NO_2 + NO_3 \xrightarrow{k_3} NO + O_2 + NO_2 \tag{2}
$$

$$
NO + NO_3 \xrightarrow{k_4} 2NO_2 \tag{3}
$$