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國立成功大學 79 學年度 化工研究所甲組 考試(物理化學試題) 共 2 頁 第 1 頁

1) A mole of steam is condensed at 100°C and the water is cooled to 0°C and frozen to ice. What is the entropy change of the water? Consider that the average specific heat of liquid water is 4.2 $J K^{-1} g^{-1}$. The heat of vaporization at the boiling point and the heat of fusion at the freezing point are 2258.1 and 333.5 $J g^{-1}$, respectively. (11%)

2). The following reaction is nonspontaneous at room temperature and endothermic: $3\,C(graphite) + 2\,H_2O(g) = CH_4(g) + 2\,CO(g)$

As the temperature is raised, the equilibrium constant will become equal to unity at some point. Estimate this temperature.

Given:

	ΔH_f°, $kJ\,mol^{-1}$			ΔG_f°, $kJ\,mol^{-1}$		
T/K	$H_2O(g)$	$CH_4(g)$	$CO(g)$	$H_2O(g)$	$CH_4(g)$	$CO(g)$
298	−241.827	−74.873	−110.529	−228.580	−50.782	−137.181
500	−243.831	−80.818	−110.022	−219.050	−32.768	−155.438
1000	−247.885	−89.881	−112.010	−192.576	19.460	−200.297
2000	−251.668	−92.462	−118.708	−135.456	130.705	−286.099

(14%)

3). Calculate the Gibbs energies of formation for gaseous and liquid H_2O if $\Delta H^\circ_{f,298} = -57.796$ and -68.315 $kcal\,mol^{-1}$ and $S^\circ_{298} = 45.104$ and 16.71 $cal\,K^{-1} mol^{-1}$, respectively. Assume $S^\circ_{298} = 31.208$ $cal\,K^{-1} mol^{-1}$ for $H_2(g)$ and 49.003 $cal\,K^{-1} mol^{-1}$ for $O_2(g)$. Calculate the vapor pressure above the liquid water at equilibrium at 298 K. (14%)

4). The following cooling curves have been found for the system antimony-cadmium.

Cd, wt.%	0	20	37.5	47.5	50	58	70	93	100
First break in curve, °C	—	550	461	—	419	—	400	—	—
Continuing constant temp. °C	630	410	410	410	410	439	295	295	321

Construct a phase diagram, assuming that no breaks other than these actually occur in any cooling curve. Label the diagram completely and give the formula of any compound formed. How many degrees of freedom are there for each area and at each eutectic point? (12%)

Note: Atomic weight: Sb = 121.75, Cd = 112.40

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5). The standard electromotive force of the cell Pt | $H_2(g)$ | HCl(ai) | AgCl(cr) | Ag has been determined from 0 to 90°C by R.G. Bates and V.E. Bower. Their data may be represented by:

$$\frac{E^\circ}{V} = 0.23659 - 4.8564\times10^{-4}\left(\frac{t}{^\circ C}\right) - 3.4205\times10^{-6}\left(\frac{t}{^\circ C}\right)^2 + 5.869\times10^{-9}\left(\frac{t}{^\circ C}\right)^3$$

What are ΔG°, ΔH°, and ΔC_p° at 25°C for the reaction

$$\frac{1}{2}H_2(g) + AgCl(cr) = HCl(ai) + Ag(cr)$$ (15%)

6). Water vapor is rapidly cooled to 25°C to find the degree of supersaturation required to nucleate water droplets spontaneously. It is found that the vapor pressure of water must be four times its equilibrium vapor pressure at 25°C. (a) Calculate the radius of a stable water droplet formed at this degree of supersaturation. (b) How many water molecules are there in the droplet? The surface tension of water at 25°C is 71.97×10^{-3} N m^{-1}. (12%)

7) The apparent activation energy for the recombination of iodine atoms in argon is -5.9 kJ mol^{-1}. This negative temperature coefficient may result from the following mechanism.

$$I + M = IM \qquad K = \frac{[IM]}{[I][M]}$$

$$IM + I \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_2 + M$$

Assuming that the first step remains at equilibrium, derive the rate equation that includes both the forward and reverse reactions. Show that the reverse reaction is bimolecular and the equilibrium constant expression for the dissociation of iodine is independent of the concentration of the third body. (12%)

8). Suppose that in an industrial batch process a substance A produces the desired product B which goes on to decay to a worthless product C, each stage of the reaction being first-order. At what time will product B be present in greatest concentration? (10%)