UNIVERSITY OF NOTRE DAME

Advanced Chemical Reaction Engineering (CBE 60546)

Prof. William F. Schneider

**NAME (PRINT):**_____

NETID (PRINT):_____

> *AS A MEMBER OF THE NOTRE DAME COMMUNITY, I WILL NOT PARTICIPATE IN OR TOLERATE ACADEMIC DISHONESTY*

SIGNED: _____

WRITE YOUR SOLUTIONS IN THE SPACE INDICATED, MAKING SURE YOUR APPROACH AND YOUR FINAL ANSWERS ARE CLEARLY INDICATED. USE THE BACK OF THE TABLES PAGES IF YOU NEED ADDITIONAL SCRATCH SPACE. WRITE YOUR NETID IN THE UPPER RIGHT OF EACH PAGE.

1 Chemical thermodynamics

One of the innovations enabling modern automotive emissions control was the introduction of an "oxygen storage" material to the catalytic converter. The function of the material is to buffer variations in oxygen pressure in the engine exhaust, so the three-way exhaust catalyst works more effectively. Doped ceria is the most common oxygen storage material, and its equilibrium reaction with O_2 can be written:

$$Ce_2O_3(s) + \tfrac{1}{2}O_2(g) \rightleftharpoons 2CeO_2(s)$$
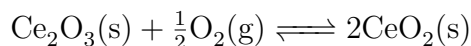
The following data were obtained for the equilibrium O_2 pressure above a mixture of solid Ce_2O_3 (MW $328\,\text{g/mol}$) and CeO_2 ($172\,\text{g/mol}$).

T (K)	P_{O_2} (Pa)	$\ln P_{O_2}/1\ \text{Pa}$
800	0.0066	-5.0
900	0.2215	-1.5

1.1   (30 pts) Determine the **standard state enthalpy**, **standard state entropy**, and **standard state Gibbs free energy** of reaction at $900\,\text{K}$. Be sure to indicate your choice of standard state and any approximations you use. You can assume that O_2 is ideal at these conditions and that the solids are phase-pure.

1. Answer

   (a) (10 pts) As solid substances, the activities of Ce_2O_3 and CeO_2 are unity. Take Pa as standard state pressure.

   $$\Delta G^\circ(900) = -R(900\,\text{K})\ln K_{eq} = -R(900\,\text{K})\ln P_{O_2}^{-1/2} = 1/2R(900\,\text{K})(-5)$$

   $$\Delta G^\circ(900) = -18.7\,\text{kJ/mol}$$

   (b) (10 pts) Two temperatures available. Use van't Hoff equation to infer ΔH:

   $$\frac{\ln K(900)}{\ln K(800)} \approx -\frac{\Delta H^\circ}{R}\left(\frac{1}{900} - \frac{1}{800}\right)$$

   $$\frac{-1/2(-1.5)}{-1/2(-5.0)} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{900} - \frac{1}{800}\right)$$

   $$\Delta H^\circ \approx 18.0\,\text{kJ/mol}$$

   (c) (10 pts) Use $\Delta G = \Delta H - T\Delta S$ to infer ΔS:

   $$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ(900)}{900\,\text{K}}$$

   $$\Delta S^\circ \approx 40.7\,\text{J/molK}$$

   $\Delta S > 0$. That's reassuring.

1.2   Suppose a closed, constant volume vessel contains $50\,g$ of Ce_2O_3 and $50\,g$ of CeO_2 in equilibrium with O_2 at $900\,K$. You introduce $0.32\,g$ O_2 into the vessel. After the vessel returns to equilibrium:

1. (10 pts) What is the pressure of O_2 in the vessel?

   (a) If the volume and temperature haven't changed, then the equilibrium pressure must be the same. $0.2215\,Pa$.

2. (10 pts) What are the masses of Ce_2O_3 and CeO_2 in the vessel?

   (a) Added $0.32\,g = 0.01\,mol\,O_2$. From stoichiometry, to consume all, must lose $0.02\,mol$ Ce_2O_3 and gain $0.04\,mol$ CeO_2:

$$m_{Ce_2O_3} = 50\,g - 0.02\,mol \times 328\,g/mol = 43.4\,g$$

$$m_{CeO_2} = 50\,g + 0.04\,mol \times 172\,g/mol = 56.9\,g$$

2   Kinetics

The acid-catalyzed hydrolysis of a cobalt fluoride complex was followed spectrophotometrically to obtain reaction lifetimes:

$$\mathrm{Co(NH_3)_5F^{2+}(aq) + H_2O \xrightarrow{H+} Co(NH_3)_5(OH)^{3+}(aq) + F^-(aq)}$$
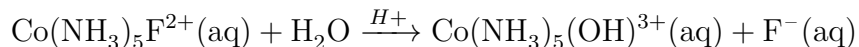
$\mathrm{Co(NH_3)_5F^{2+}}$ (M)	$\mathrm{H^+}$ (M)	$t_{1/2}$ (hr)	$t_{1/4}$ (hr)
0.1	0.01	1	2
0.2	0.01	1	2
0.1	0.02	0.5	1

2.1   (50 pts) Provide as much information as you can about the reaction rate law based on the available data.

1. (10 pts) H_2O in large excess. No information about its contribution to rate. H^+ is a catalyst. Concentration doesn't change. In absence of other information, assume products don't influence rate. Postulate

$$r = kC_{\mathrm{CoF^{2+}}}^{\alpha} C_{\mathrm{H^+}}^{\beta}$$

2. (15 pts) From first and second experiments, doubling $C_{\mathrm{CoF^{2+}}}$ at constant $C_{\mathrm{H^+}}$ does not change half-life. Must have $\alpha = 1$.

$$r = kC_{\mathrm{CoF^{2+}}}^{1} C_{\mathrm{H^+}}^{\beta}$$

3. (15 pts) From first and third experiments, doubling H^+ at constant CoF^{2+} halves half-life. Because $C_{\mathrm{H^+}}$ is a constant:

$$t_{1/2} = \frac{\ln 2}{kC_{\mathrm{H^+}}^{\beta}}$$

$$\beta = 1$$

$$r = kC_{\mathrm{CoF^{2+}}}^{1} C_{\mathrm{H^+}}^{1}$$

4. (10 pts) Can estimate k from any one of the experiments.

$$t_{1/2} = \frac{\ln 2}{kC_{\mathrm{H^+}}}$$

$$k = \frac{\ln 2}{t_{1/2}C_{\mathrm{H^+}}} = \frac{\ln 2}{1\,\mathrm{hr} \times 0.01\,\mathrm{M}} = 69\,\mathrm{/mol/hr}$$

3 Tables & Equations

balanced reaction	$\sum_j \nu_j A_j = 0$
advancements	$n_j = n_{j0} + \sum_i \nu_{ij} \xi_i$
standard potentials	$G = H - TS$
reaction free energy	$G(\xi) = \sum_j n_j \mu_j$
chemical potential	$\mu_j = \mu_j^{\circ}(T) + RT \ln a_j$
chemical equilibrium	$\partial G / \partial \xi = 0$
mass action expression	$Q(\xi) = \prod_j a_j^{\nu_j}$
equilibrium constant	$K_{eq}(T) = \exp(-\Delta G^{\circ}(T)/RT)$
Gibbs-Helholtz	$\partial(G/T)/\partial T = -H/T^2$
van't Hoff	$\partial \ln K / \partial(1/T) = -\Delta H^{\circ}(T)/R$
First-order reaction	$r = k C_A \; C_A = C_{A0} e^{-kt} \; t_{1/2} = \ln 2/k$
Second-order reaction	$r = k C_A^2 \; 1/C_A = 1/C_{A0} - kt \; t_{1/2} = 1/C_{A0}k$

Table 1: Key units

N_{Av}:	6.02214×10^{23}	mol^{-1}		
1 amu:	1.6605×10^{-27}	kg		
k_{B}:	1.38065×10^{-23}	J K^{-1}	8.61734×10^{-5}	eV K^{-1}
R:	8.314472	J K^{-1} mol^{-1}	8.2057×10^{-2}	l atm mol^{-1} K^{-1}
σ_{SB}:	5.6704×10^{-8}	J s^{-1} m^{-2} K^{-4}		
c:	2.99792458×10^8	m s^{-1}		
h:	6.62607×10^{-34}	J s	4.13566×10^{-15}	eV s
$\hbar$:	1.05457×10^{-34}	J s	6.58212×10^{-16}	eV s
hc:	1239.8	eV nm		
e:	1.60218×10^{-19}	C		
m_e:	$9.10938215 \times 10^{-31}$	kg	1: 0.5109989	MeV c^{-2}
ϵ_0:	8.85419×10^{-12}	C^2 J^{-1} m^{-1}	5.52635×10^{-3}	e^2 Å^{-1} eV^{-1}
$e^2/4\pi\epsilon_0$:	2.30708×10^{-28}	J m	14.39964	eV Å
a_0:	0.529177×10^{-10}	m	0.529177	Å
E_{H}:	1	Ha	27.212	eV