



UNIVERSITY OF  
NOTRE DAME

Advanced Chemical Reaction Engineering  
(CBE 60546)

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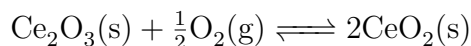
*AS A MEMBER OF THE NOTRE DAME COMMUNITY, I WILL NOT  
PARTICIPATE IN OR TOLERATE ACADEMIC DISHONESTY*

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:



The following data were obtained for the equilibrium  $O_2$  pressure above a mixture of solid  $Ce_2O_3$  (MW 328 g/mol) and  $CeO_2$  (172 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 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.

$$\Delta G^\circ(900) = -R(900 \text{ K}) \ln K_{eq} = -R(900 \text{ K}) \ln P_{O_2}^{-1/2} = 1/2 R(900 \text{ K})(-1.5)$$

$$\Delta G^\circ(900) = -5.6 \text{ kJ/mol}$$

- (b) (10 pts) Two temperatures available. Use van't Hoff equation to infer  $\Delta H$ :

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

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

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

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

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

$$\Delta S^\circ \approx -14 \text{ J/molK}$$

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

1.2 Suppose a closed, constant volume vessel contains 50 g of  $\text{Ce}_2\text{O}_3$  and 50 g of  $\text{CeO}_2$  in equilibrium with  $\text{O}_2$  at 900 K. You introduce 0.32 g  $\text{O}_2$  into the vessel. After the vessel returns to equilibrium:

1. (10 pts) What is the pressure of  $\text{O}_2$  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  $\text{Ce}_2\text{O}_3$  and  $\text{CeO}_2$  in the vessel?

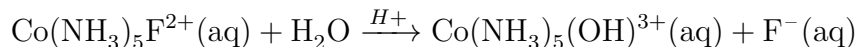
(a) Added 0.32 g = 0.01 mol  $\text{O}_2$ . From stoichiometry, to consume all, must lose 0.02 mol  $\text{Ce}_2\text{O}_3$  and gain 0.04 mol  $\text{CeO}_2$ :

$$m_{\text{Ce}_2\text{O}_3} = 50 \text{ g} - 0.02 \text{ mol} \times 328 \text{ g/mol} = 43.4 \text{ g}$$

$$m_{\text{CeO}_2} = 50 \text{ g} + 0.04 \text{ mol} \times 172 \text{ g/mol} = 56.9 \text{ g}$$

## 2 Kinetics

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



$\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ (M)	$\text{H}^+$ (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.

- (10 pts)  $\text{H}_2\text{O}$  in large excess. No information about its contribution to rate.  $\text{H}^+$  is a catalyst. Concentration doesn't change. In absence of other information, assume products don't influence rate. Postulate

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

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

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

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

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

$$\beta = 1$$

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

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

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

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

### 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-Helmholtz	$\partial(G/T) / \partial T = -H/T^2$
van't Hoff	$\partial \ln K / \partial(1/T) = -\Delta H^\circ(T)/R$
First-order reaction	$r = kC_A \quad C_A = C_{A0}e^{-kt} \quad t_{1/2} = \ln 2/k$
Second-order reaction	$r = kC_A^2 \quad 1/C_A = 1/C_{A0} - kt \quad t_{1/2} = 1/C_{A0}k$

**Table 1:** Key units

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