

10.40 Thermodynamics

Fall 2003

Problem Set 11

 Problem 2

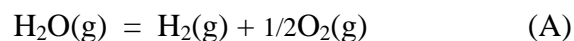
Hydrogen is being considered for widespread deployment as a primary energy carrier. A key motivation for this is to avoid the production and emissions of carbon dioxide associated with the combustion of fossil fuels in power plants and transportation equipment. To achieve this goal, a transition to a non-fossil based primary energy supply system is required. One option is to use nuclear power for supplying all our electricity, heating and transportation fuel needs.

In this problem, you are to address the issues raised in parts a-d below in analyzing the effectiveness of three proposed approaches for using nuclear power to produce hydrogen. In all three approaches a new Generation IV fission reactor that uses a high temperature helium gas cooled cycle will be used to provide the energy source in the form of heat and/or electric power. The three approaches are:

1. **Direct thermolysis** using heat to directly split water into hydrogen and oxygen.
2. **High temperature electrolysis** using electricity to electrolyze water.
3. **Thermochemically** using heat in a multi-step cycle.

In answering parts a-d below please clearly state all assumptions made.

- (a) Referring to approach (1.), helium gas is circulated through the reactor core where it is heated to 850°C. Using a helium gas stream at this temperature as a means to heat steam, estimate the maximum fraction of steam at 1 bar that will be decomposed by the direct thermolysis reaction:



Assuming that only reaction (A) occurs, at what temperature would you expect the conversion to hydrogen to be 50% complete? Would increasing the pressure to 200 bar have a measurable effect on conversion at this temperature? If so, describe how you would calculate it.

- (b) Referring to approach (2.), the addition of electrical work in a properly designed electrolysis cell with Pt electrodes will catalytically decompose water to hydrogen and oxygen as given in reaction A. Estimate the minimum amount of electrical power that would be required to produce 20 moles of hydrogen per second by electrolysis carried out at 850°C and 1 atm.
- (c) In a practical electrolysis process, transport and kinetic limitations increase the required power to 1.5 times the minimum from part (b). Assuming that helium gas at 850°C is fed to the power cycle, estimate the absolute minimum rate of heat transfer from the reactor core needed to supply the required electrical power. An average ambient temperature for heat

rejection of 25°C can be assumed.

(d) Referring to approach (3.), the following 3-step thermochemical cycle using iodine (I) and sulfur (S) based intermediates has been proposed by General Atomics:

1. $\text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{HI} + \text{H}_2\text{SO}_4$
2. $2\text{HI} = \text{H}_2 + \text{I}_2$
3. $\text{H}_2\text{SO}_4 = \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2$

where all components are in a gaseous state. In their process, liquid water is supplied at 25°C and H_2 and O_2 are produced at 25°C which is also the ambient temperature. General Atomics rates the efficiency of their overall 3-step process at 0.47-- defined as the ratio of the heating value of the net H_2 produced to the heat input from the reactor helium loop. To justify whether 0.47 (or 47%) is a thermodynamically acceptable value, estimate the maximum efficiency of the process assuming all reactions in the cycle go to completion. Note that the net cycle given by reactions (1-3) is equivalent to reaction (A) given in part (a).

Data:

Heat capacities of steam ($\text{H}_2\text{O}(\text{g})$), $\text{He}(\text{g})$, $\text{H}_2(\text{g})$, and $\text{O}_2(\text{g})$ can be assumed constant with the following values:

$$\begin{aligned} C_p(\text{H}_2\text{O}(\text{g})) &= 43.95 \text{ J/mol K} \\ C_p(\text{H}_2(\text{g})) &= 29.3 \text{ J/mol K} \\ C_p(\text{O}_2(\text{g})) &= 29.3 \text{ J/mol K} \\ C_p(\text{He}(\text{g})) &= 20.8 \text{ J/mol K} \end{aligned}$$

Standard Gibbs energy and enthalpy of formation of water:

$\Delta G_f^\circ(\text{H}_2\text{O}(\text{g})) = -228.8 \text{ kJ/mol}$ and $\Delta H_f^\circ(\text{H}_2\text{O}(\text{g})) = -241.9 \text{ kJ/mol}$ with standard states taken as ideal gas at 1 atm, 298.15 K.

Enthalpy of vaporization of pure water at 25°C $= \Delta H_{\text{vap}} = 2442.5 \text{ kJ/kg}$

See also Appendix G and Figures 8.11a and 8.11b in *Thermodynamics and its Applications*, 3rd ed. for additional property data.

Solution:

(a)

Since the reaction takes place at a high temperature (850°C) and a low pressure (1 bar), we can make the following assumptions when modeling hydrogen conversion.

Assumptions

1. Ideal gas behavior for H_2O , H_2 , O_2 mixture
2. Single phase
3. Maximum hydrogen conversion occurs at chemical equilibrium

The mole fractions of the mixture components can be related to the Gibbs Free Energy of reaction by

$$K_a = \exp\left(\frac{\Delta G_{rxn}^0}{RT}\right) \quad (16-26)$$

$$\text{where } K_a \equiv \prod_{j=1}^{n'} \left(\frac{\hat{f}_j}{f_j^0}\right)^{\nu_j} = \left(\prod_{j=1}^{n'} \hat{\phi}_j^{\nu_j}\right) \left(\prod_{j=1}^{n'} y_j^{\nu_j}\right) P^{\nu} = K_{\phi} K_y P^{\nu} \quad (1)$$

since all components of the reaction will be present as vapors and all f_j^0 have been taken as unit fugacity. With the ideal gas assumption, all $\hat{\phi}_j^0 = 1$. For reaction (A),

$$K_a = K_{\phi} K_y P^{\nu} = \frac{y_{H_2} (y_{O_2})^{1/2}}{y_{H_2O}} P^{1/2} \quad (2)$$

Using the extent of reaction, ξ , to define the mole fractions, on a per mole of water entering the reactor basis yields,

$$y_{H_2O} = \frac{1-\xi}{1+1/2\xi}; \quad y_{H_2} = \frac{\xi}{1+1/2\xi}; \quad y_{O_2} = \frac{1/2\xi}{1+1/2\xi} \quad (3)$$

Combining Eq. (3) with (2),

$$K_a = \frac{\xi^{3/2}}{(2+\xi)^{3/2}(1-\xi)} P^{1/2} \quad (4)$$

In order to solve for the equilibrium extent of reaction, we need to solve for the other part of Eq. (16-26), the change in Gibbs Free Energy at 850 °C. Since all of our data is at 25 °C, we need to use Eq. (16-43) to determine the temperature dependence of the Gibbs Free Energy.

$$\frac{d \ln K_a}{dT} = -\frac{1}{R} \frac{d\left(\frac{\Delta G_{rxn}^0}{T}\right)}{dT} = \frac{\Delta H_{rx}^0}{RT^2} \quad (16-43)$$

Rearranging and integrating,

$$\frac{\ln K_a(T)}{\ln K_a(T^0)} = \int_{T^0}^T \frac{\Delta H_{rx}^0}{RT^2} dT \quad (5)$$

In order to integrate, we need ΔH_{rx}^0 as a function of T .

$$\Delta H_{rx}^0(T) = \Delta H_{rx}^0(T^0) + \int_{T^0}^T \Delta C_{p,rx}^0 dT \quad (6)$$

$$\text{but } \Delta C_{p,rx}^0 = \sum v_i C_{p,i}^0 = C_{p,H_2}^0 + \frac{1}{2} C_{p,O_2}^0 - C_{p,H_2O}^0 = 29.3 + \frac{1}{2}(29.3) - 43.95 = 0$$

$$\text{so } \Delta H_{rx}^0 = 241.9 \text{ kJ/mol} \neq f(T)$$

Integrating Eq. (5) yields

$$\frac{\ln K_a(T)}{\ln K_a(T^0)} = -\frac{\Delta H_{rx}^0}{R} \left(\frac{1}{T} - \frac{1}{T^0} \right) \quad (7)$$

$$\ln K_a(T^0) = -\frac{\Delta G_{rx}^0(T^0)}{RT^0} = -92.3 \quad (8)$$

Evaluating Eq. (7) yields

$$K_a(850^\circ\text{C}) = 1.1E-9 \quad (10)$$

which means that the mixture is essentially pure water. Combining Eqs. (4) and (10) and solving for extent of reaction,

$$K_a = \frac{\xi^{3/2}}{(2+\xi)^{3/2}(1-\xi)} (1 \text{ bar})^{1/2} = 1.1E-9$$

$$\xi = 1.3E-6 = \text{fraction of steam converted to } H_2 \quad (11)$$

50% Conversion

At 50% conversion of H_2O , $\xi = 1/2$

$$y_{H_2O} = \frac{0.5}{1.25} = 0.4$$

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$$y_{O_2} = \frac{0.25}{1.25} = 0.2$$

$$K_a = \frac{0.4(0.2)^{1/2}}{0.4} = 0.447 \quad (12)$$

$$\ln K_a = -0.805$$

Plugging Eq. (12) into (7) and solving for T yields

$$T = 4780K$$

This temperature is so high that the water would almost be low-temperature plasma. Direct thermolysis is not a good method for hydrogen production.

For the case of 200 bar and 850°C, we still evaluate the ΔG_{rxn}^0 at 1 bar and 850°C, so it is unchanged from the previous part of this problem. As the pressure increases to 200 bar, we need to consider whether K_ϕ deviates from 1 and not the effect of P^v . In this case $v=+1/2$.

$$K_a = K_\phi K_y P^v = \left(\frac{\hat{\phi}_{H_2} (\hat{\phi}_{O_2})^{1/2}}{\hat{\phi}_{H_2O}} \right) \left(\frac{y_{H_2} (y_{O_2})^{1/2}}{y_{H_2O}} \right) P^{1/2} \quad (13)$$

So the by the P^v effect, pressure tends to drive reaction (A) to the left. To be sure about this effect, we need values of K_ϕ which will require some type of mixture equation of state, such as PREOS with δ_{ij} and mixing rules. As a first step, let's use the Lewis and Randall rule (Eq. (9-196)) and corresponding states.

$$\hat{f}_i = y_i f_i(\text{pure}) \quad \text{all T, P of mixture} \quad (14)$$

$$\hat{\phi}_i \equiv \frac{\hat{f}_i}{P} = y_i \left(\frac{f_i}{P} \right) \quad (15)$$

The fugacity coefficients can be found from a corresponding state type chart of fugacity/pressure as a function of the reduced pressure. Such a chart yielded the following results for T=850°C and P=200 bar:

	T _c (K)	T _r	P _c (bar)	P _r	ϕ _i
H ₂	33	34	12.9	15.5	1.0
O ₂	154	7.29	50	4	1.0
H ₂ O	647.3	1.74	221	0.91	0.96

$$K_\phi = 1.04$$

$$K_a = \exp\left(\frac{\Delta G_{rxn}^0}{RT}\right) = 1.04(200)^{1/2} K_y = 14.7K_y$$

So conversion decreases significantly at the higher pressure.

(b)

For a fully reversible process, the minimum work is $\Delta B = \Delta G$ ($T = \text{const} = 850^\circ\text{C}$).

$$\text{From part (a), } \Delta G_{rxn}^0 = -RT \ln K_a = -(8.314 \text{ J/molK})(850 + 273)(-20.6) = 192.5 \text{ kJ/mol}$$

$$\dot{W}_{\min} = \dot{m}_{H_2} \Delta G_{rxn}^0 = (20 \text{ mol/s})(192.5 \text{ kJ/mol}) = 3.85 \text{ E}6 = 3.85 \text{ MWatts}$$

(c)

In order to estimate the absolute minimum rate of heat transfer, we assume that an infinite supply of hydrogen at 850°C is available for the process. The required power is equal to 1.5 times the minimum from part (b),

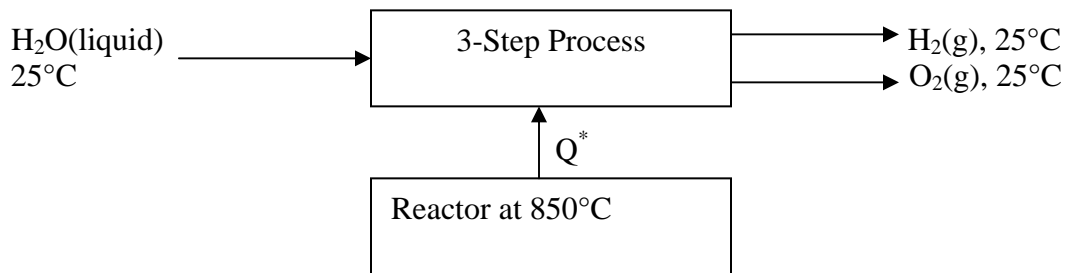
$$\dot{W} = 1.5 \Delta G_{rxn}^0 = 5.78 \text{ MWatts}$$

In order to extract the maximum work from our heat resource, we use a Carnot engine which rejects heat to a reservoir at 25°C .

$$\dot{Q}_{H,\min} = \frac{\dot{W}_{Carnot}}{\eta_{Carnot}} = \frac{\dot{W}_{Carnot}}{\frac{T_H - T_C}{T_H}} = \frac{5.78 \text{ MWatts}}{0.73} = 7.9 \text{ MWatts}$$

(d)

Basis: 1 mol of water fed and reacted to make 1 mol of hydrogen



$$Q^* \equiv \text{process heat supplied} = \Delta H_{vap} + \Delta H_{rxn} (H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g))$$

$$\eta_{Process}^{max} = \left| \frac{\Delta H_{H_2, combustion}}{Q^*} \right| = \frac{\Delta H_{rxn}}{\Delta H_{rxn} + \Delta H_{vap}} = \frac{1}{1 + \frac{\Delta H_{vap}}{\Delta H_{rxn}}} = \frac{1}{1 + \frac{2442.5 \text{ kJ/kg} (18 \text{ kg/mol}) E-3}{241.9 \text{ kJ/kg}}} = 0.846$$

General Atomics efficiency of 47% is thermodynamically viable since it is less than the maximum thermodynamically allowed value of 85%.