

October 3, 2017 Time Allowed: 40 minutes

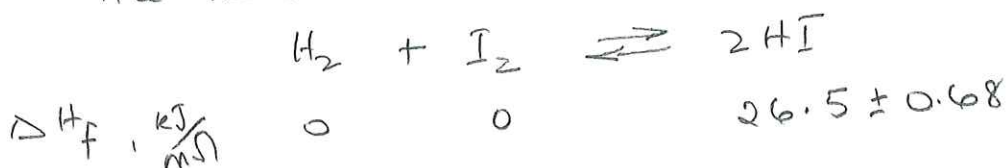
a)

Pure hydrogen iodide (HI) is produced by reacting hydrogen (H_2) and iodine (I_2). The reaction is reversible. At 424.85°C , the equilibrium constant (K_p) is given as 54.35. If stoichiometric amounts of hydrogen and iodine are introduced into a closed vessel that was initially empty, and the pressure is maintained at 2 atm.,

- What are the mole fractions of the compounds in the vessel at equilibrium when the temperature is maintained at 424.85°C ?
- If the vessel temperature suddenly dropped to and is maintained at 350°C , what would the mole fraction of iodine in vessel be and what is the error in its value?

Data: The Heat of formation of HI (gas) is given as $26.5 \pm 0.68 \text{ kJ/mol}$; the universal gas constant R is 8.314 J/mol K . The van't Hoff equation is $\ln(K_{p2}/K_{p1}) = (\Delta H_r/R) \{1/T_1 - 1/T_2\}$.

The reaction is



The heat of reaction is $2(26.5) = 53 \text{ kJ/mole}$
and the error is $2(0.68) = \pm 1.36 \text{ kJ/mole}$.

$$\Delta H_r = 53 \pm 1.36 \text{ kJ/mol}$$

Assume 1 mole of each of H_2 and I_2 are charged into the reactor. After time t , let x moles of I_2 be the amount consumed. $(1-x)$ moles of each of H_2 and I_2 remain and $2x$ moles of HI is formed. The total moles in the vessel remains constant = 2 moles.

$$(a) \text{ At } 424.85^\circ\text{C} \text{ or } 698 \text{ K},$$

$$K_p = 54.35 = \frac{\bar{P}_{HI}^2}{\bar{P}_{H_2} \bar{P}_{I_2}} = \frac{(x)^2}{\left(\frac{1-x}{2}\right)^2} = \frac{4x^2}{(1-x)^2}$$

$54.35(1-x^2) = 4x^2$. This is a quadratic
and $x = 0.7866$ and 1.3723 . The higher
value is not acceptable. $\therefore x = 0.7866$.

mole fractions

$$H_2 = \frac{1 - 0.7866}{2} = 0.1067 \quad ; \quad I_2 = H_2 = 0.1067$$

$$HI = 0.7866 \quad \sum = 1.0 \quad \rightarrow$$

(b) At 350°C or 623.15 K , the equilibrium constant K_p is different. from the van't Hoff equation,

$$\ln \frac{K_{p2}}{K_{p1}} = \frac{\Delta H_r}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad ; \quad T \text{ in Kelvin}$$

With the lower value of ΔH_r or 51.64 kJ/mol ,

$$\ln \frac{K_{p2}}{54.35} = \frac{51.64 (10^3)}{8.314} \left[\frac{1}{698} - \frac{1}{623.15} \right]$$

$$= -1.0689$$

$$\therefore K_{p2} = \exp(-1.0689)(54.35) = 18.66$$

Hence, from the definition for K_p ,

$$18.66(1-x)^2 = 4x^2 \Rightarrow x_L = 0.6835 \text{ or } 1.8622$$

The higher value is unacceptable.

With the higher value of ΔH_r or 54.36 kJ/mol ,

$$\ln \frac{K_{p2}}{54.35} = \frac{54.36 (10^3)}{8.314} \left[\frac{1}{698} - \frac{1}{623.15} \right]$$

$$= -1.1252$$

$$\therefore K_{p2} = 17.6415$$

$$\text{and } 17.6415(1-x)^2 = 4x^2 \Rightarrow x_H = 0.6774 \text{ or } 1.9090$$

$$\bar{x} = \frac{x_L + x_H}{2}, \quad \pm \Delta x = \left| \frac{x_L - x_H}{2} \right| \Rightarrow x = 0.6805 \pm 0.00305$$

$$\square \text{ Mole fraction for } I_2 = \frac{1 - 0.6805}{2} \pm \frac{0.00305}{2} \Rightarrow 0.1598 \pm 0.00153$$