

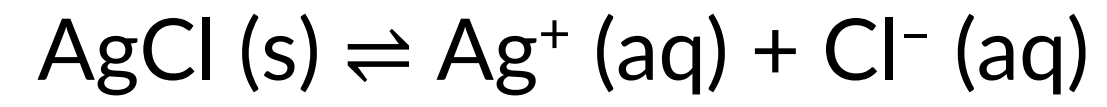


# THERMODYNAMICS

GIBBS FREE ENERGY (G) AND EQUILIBRIUM

CHEMISTRY 165 // SPRING 2020

# PRACTICE PROBLEM 1

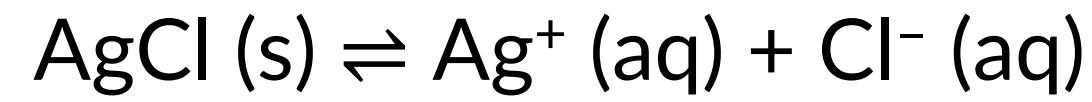


Given the following standard free energies of formations, calculate the solubility product ( $K_{sp}$ ) for AgCl at 298.15 K.

	AgCl (s)	Ag <sup>+</sup> (aq)	Cl <sup>-</sup> (aq)
$\Delta G_f^\circ \left( \frac{\text{kJ}}{\text{mol}} \right)$	-109.8	77.1	-131.2

— answer —

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— answer —

First, calculate the standard Gibbs free energy change.

$$\begin{aligned}\Delta G_{\text{rxn}}^\circ &= \sum n_{\text{prod}} \Delta G_{f,\text{prod}}^\circ - \sum n_{\text{react}} \Delta G_{f,\text{react}}^\circ \\ &= \left[ (1 \text{ mol Ag}^+) \times \left( 77.1 \frac{\text{kJ}}{\text{mol}} \right) + (1 \text{ mol Cl}^-) \times \left( -131.2 \frac{\text{kJ}}{\text{mol}} \right) \right] - (1 \text{ mol AgCl}) \times \left( -109.8 \frac{\text{kJ}}{\text{mol}} \right) \\ \Delta G_{\text{rxn}}^\circ &= 55.7 \text{ kJ}\end{aligned}$$

Then, calculate the equilibrium constant ( $K_{sp}$ ).

$$\begin{aligned}K_{sp} &= e^{\frac{-\Delta G_{\text{rxn}}^\circ}{RT}} \\ &= e^{\frac{-(55.7 \text{ kJ})}{\left( 8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) (298.15 \text{ K})}}\end{aligned}$$

$$K_{sp} = 1.74 \times 10^{-10}$$

## PRACTICE PROBLEM 2

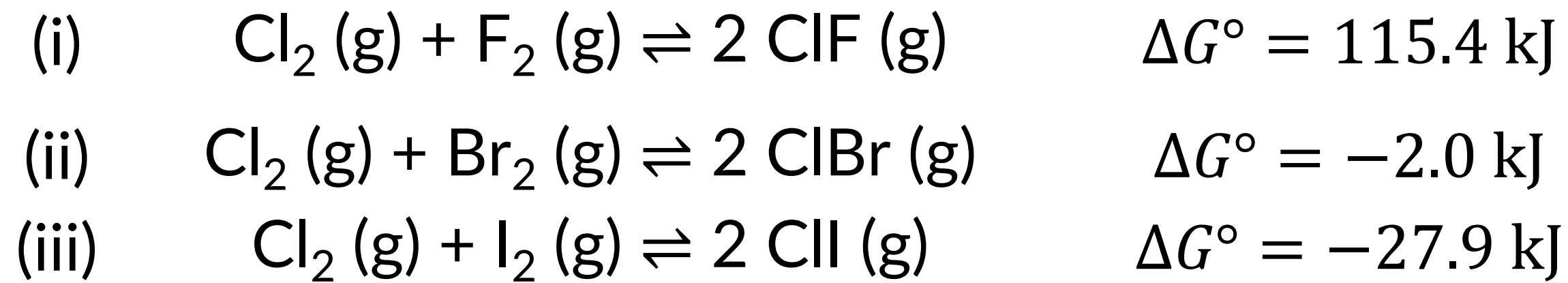
Which of the following reactions has the largest value of  $K_p$  at 25 °C?



— answer —

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— answer —

Recall that the standard Gibbs free energy change can be related to the equilibrium constant via:

$$K = e^{\frac{-\Delta G^\circ}{RT}} \quad \text{or} \quad \Delta G^\circ = -RT \ln K \quad \text{or} \quad \ln K = \frac{\Delta G^\circ}{RT}$$

Qualitatively, we know that a large  $K_p$  value means that the equilibrium is products-favored.

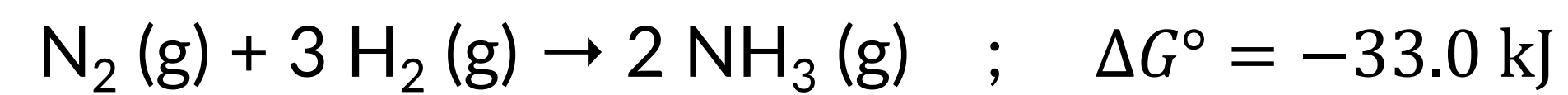
This would correspond to a very negative (very spontaneous, products favored equilibrium) value of  $\Delta G^\circ$ .

So, the answer is **reaction (iii)**, which has:

$$\begin{aligned} K_p &= e^{\frac{-\Delta G_{\text{rxn}}^\circ}{RT}} \\ &= e^{\frac{-(-27.9 \text{ kJ})}{\left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298.15 \text{ K})}} \end{aligned}$$

$$K_p = 7.8 \times 10^4$$

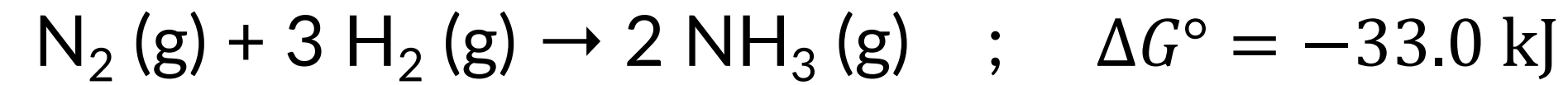
## PRACTICE PROBLEM 3



What is the value of  $\Delta G$  when  $P_{\text{N}_2} = P_{\text{H}_2} = P_{\text{NH}_3} = 0.870 \text{ atm}$  and  $T = 298 \text{ K}$ ?

— *answer* —

## PRACTICE PROBLEM 3



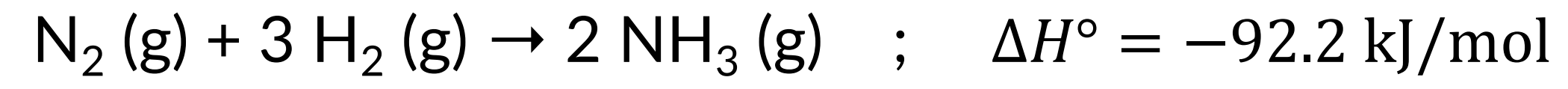
What is the value of  $\Delta G$  when  $P_{\text{N}_2} = P_{\text{H}_2} = P_{\text{NH}_3} = 0.870 \text{ atm}$  and  $T = 298 \text{ K}$ ?

— *answer* —

We can use the following relationship to find the nonstandard Gibbs free energy change:

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q \\ &= \Delta G^\circ + RT \ln \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} \\ &= -33.0 \text{ kJ} - \left(0.008314 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}\right) (298 \text{ K}) \ln \frac{(0.870)^2}{(0.870)(0.870)^3} \\ \Delta G &= -32.3 \text{ kJ}\end{aligned}$$

## PRACTICE PROBLEM 4



(a) If the temperature is increased, how will the value of  $K_p$  change?

(b) If  $K_p = 41$  at 400 K, what is the value of  $K_p$  at 700 K?

— *answer* —



## PRACTICE PROBLEM 4



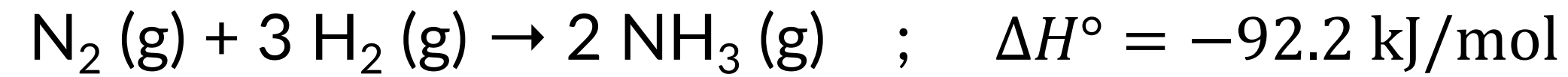
(a) If the temperature is increased, how will the value of  $K_p$  change?

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(a) Because the reaction is exothermic, we can treat heat as a product. Invoking Le Chatelier's Principle, increasing the temperature will **decrease the value  $K$** .

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— answer —

(a) Because the reaction is exothermic, we can treat heat as a product. Invoking Le Chatelier's Principle, increasing the temperature will **decrease the value  $K$** .

(b) We can calculate the value of  $K$  at a different temperature using:

$$\begin{aligned}\ln \frac{K_{700}}{K_{400}} &= -\frac{\Delta H^\circ}{R} \left[ \frac{1}{T_{700}} - \frac{1}{T_{400}} \right] \\ \ln K_{700} - \ln K_{400} &= -\frac{\Delta H^\circ}{R} \left[ \frac{1}{T_{700}} - \frac{1}{T_{400}} \right] \\ \ln K_{700} - \ln (41) &= -\frac{-92.2 \frac{\text{kJ}}{\text{mol}}}{0.008314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left[ \frac{1}{700 \text{ K}} - \frac{1}{400 \text{ K}} \right] \\ \ln K_{700} &= -8.168 \\ K_{700} &= 2.8 \times 10^{-4}\end{aligned}$$