FROM LAST TIME

\[ \ln \frac{K_2}{K_1} = -\frac{\Delta H^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

\[ \Delta H^o = \left( \ln \frac{K_2}{K_1} \right) \left( -R \right) \]

\[ = -R \frac{2.303 (\log K_2 - \log K_1)}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{-R \cdot 2.303 \log \frac{K_2}{K_1}}{\frac{1}{T_2} - \frac{1}{T_1}} \]

\[ T_1 = 298 \]

\[ T_2 = 299 \]

\[ \Delta \phi_{\text{nu}} = -0.029 \]

\[ = -2.303 R \frac{pK_2 - pK_1}{\frac{1}{T_2} - \frac{1}{T_1}} \]

\[ = 2.303 \left( \frac{8.31 \text{ J/K mol}}{299 K} \right) (-0.029) = \frac{49450 \text{ J/mol}}{298 K} \]

\[ = 49 \text{ kJ/mol} \]

Problem

4.13 → Good coupled equilibrium question

[Diagram: Greble - Thu 1:00p]
Chapter 4
Problems: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 30, 32a

Chapter 5 - Free Energy and Physical Equilibria

And coupling chemical to physical

Think of a reaction which increases a gas volume

\[ \text{A(g)} \rightarrow \text{B(g)} + \text{C(g)} \]

We can couple this to doing work.
You can look at this in reverse.

Q: If all is at equilibrium and you push on the piston, what happens?

A: Le Chatelier says some B + C will go back to A.

Conclusion: Can (must) couple chemical and physical equilibria

Physical Effects:
Pressure, surface tension, chemical or charge gradient across a membrane, phase changes
Equilibrium → "A state where nothing happens"

\[ \Delta \mu^0 = 0 \]

(Non-equilib) Spontaneous processes have \( \Delta \mu \neq 0 \)

\[ \mu_{H_2O(g)} = \mu_{H_2O(l)} \text{ at equilibrium} \]

Since \( \mu = \mu_0 + RT \ln a \) then if we refer to the same standard state \( \mu_0 \)

True for any phase relationship

\[ a_{\text{phase 1}} = a_{\text{phase 2}} \text{ at equilibrium} \]

In the above case

\[ \Delta \mu_{H_2O(g)} = P_{H_2O(g)} \]

\[ K = \frac{a_{H_2O(g)}}{a_{H_2O(l)}} \]

\[ \Delta H_{\text{eq}} = 1.0 \text{ (pure liquid)} \]

Van't Hoff

\[ \ln \frac{K_2}{K_1} = \frac{-\Delta H_{\text{eq}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \text{ Temp. Dependence} \]

becomes Clausius-Clapeyron

\[ \ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{eq}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \text{ DUH!} \]
"Boiling" occurs when $P_{H_2O(g)}$ reaches the total external pressure.

**Hiking:**

Q: You find that at some mountain peak, pure water boils at 75°C. What is the air pressure?

$$\ln \frac{P}{1 \text{ atm}} = \frac{-\Delta H_{\text{vap}}}{R} \left( \frac{1}{75 + 273} - \frac{1}{100 + 273} \right)$$

$$= 0.38 \text{ atm} \quad (20,320 \text{ feet})$$

Q: What assumption?

A: $\Delta H$ known and independent of temperature.

**Phase Diagram**

$\log P$ vs. $\log T$ (K)

- Measured boiling points
- Liquid and gas

Good for liquid and gas

- Line of $\Delta H^0$ independent of $T$

**Ternary Diagram**

- Solid
- Liquid
- Vapor
- Critical Point
- Triple Point

$log P$ vs. $T$