10/10/01

FROM LAST TIME

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

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

$$= \frac{-R\,2.303(\log K_2 - \log K_1)}{\frac{1}{T_2}-\frac{1}{T_1}} = \cancel{-R(2.303)\log K_2/K_1}$$

$T_1 = 298$

$\downarrow$

$T_2 = 299$

$\Delta pK_a =$

-0.029

$$= \frac{2.303R(pK_2 - pK_1)}{\frac{1}{T_2}-\frac{1}{T_1}}$$

$$= \frac{2.303(8.31\ \mathrm{J\,K^{-1}\,mol^{-1}})(-0.029)}{\frac{1}{299\,K}-\frac{1}{298\,K}} = 49450\ \mathrm{J/mol}$$

$$= 49\ \mathrm{kJ/mol}$$

Problem

4.13 → Good coupled equilib question)

Gretche

Thu 1:00p

Free Energy and Chemical Equilibria

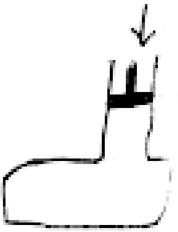
Chapter 4 Problems: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 30, 32a

Chapter 5 – Free Energy and Physical Equilibria

And coupling chemical to physical

Think of a reaction which increases a gas volume

$$A(g) \rightarrow B(g) + C(g)$$



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

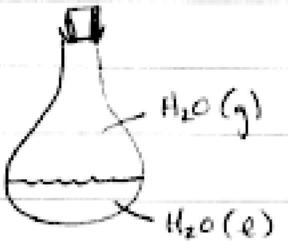
From before:

(apparently) N.B

(on average)

$\Delta\mu_{T,P} = 0$ ← Equilibrium ⇒ " A state where nothing happens "

(Non-equilib) Spontaneous processes have $\Delta\mu_{T,P} \leq 0$



$\mu_{H_2O(g)} = \mu_{H_2O(l)}$ at equilibrium

Since $\mu = \mu_0 + RT \ln a$
then

if we refer to the same
standard state (μ_0)
then

$a_{H_2O(g)} = a_{H_2O(l)}$

True for any phase
relationship
a (phase 1) = a (phase 2)
at equilibrium

partial pressure

In the above case $a_{H_2O(g)} \simeq P_{H_2O(g)}$

$K = \frac{a_{H_2O(g)}}{a_{H_2O(l)}} = P$ $a_{H_2O(l)} = 1.0$ (pure liquid)

Van't Hoff

$$\ln \frac{K_2}{K_1} = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$ Temp-Dependence

becomes Clausius-Clapeyron

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$ DUH!

"Boiling" Occurs when $P_{H_2O(g)}$ reaches the total external pressure.

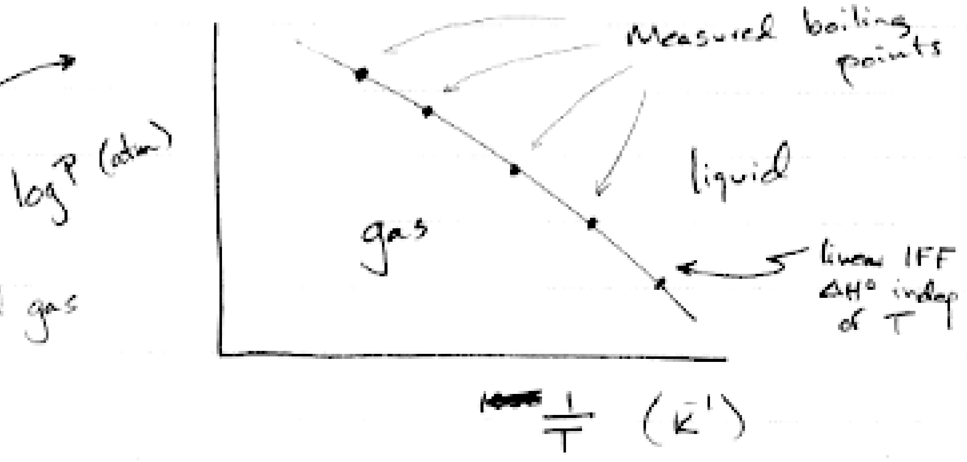
Hiking: Q: You find that at some mountain peak, pure water boils at 75°C. What is the air pressure?

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

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

Q: What assumption?
A: ΔH known and independent of temperature

Phase Diagram



GOOD FOR liquid and gas