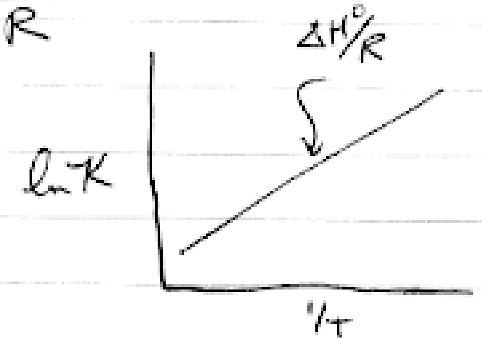
10/5/01 ①

$$\begin{array}{r}10.06\\ -5.42\\ \hline 4.64\end{array}$$

VAN'T HOFF $$\frac{d \ln K}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H^\circ}{R}$$



IF $\Delta H^\circ < 0$ (exothermic)
then

K↑ as T↓

or

Think LeChatelier K↓ as T↑

Exothermic: A + B ⇌ C + D + heat

Makes sense: increase T, reaction should go to the left (K↓)

IF
ΔH° constant w/ T
THEN

$$\int d \ln K = -\frac{\Delta H^\circ}{R} \int d\left(\frac{1}{T}\right)$$

$$K_2 - K_1 = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_0}\right)$$

Another, more common, form of Van't Hoff

N.B. [BUT only if ΔH° is independent of T

Often OK for limited ranges of T

Not good for processes with large ΔC_p

Skip Galvanic Cells pp 153-160
but good example
of biologically relevant (respiratory chain)
non-PV work.

161 and onward - good word problem
examples to review

Example 4.12 - T-dependence of Tris pKa

$$\mathrm{TrisH^+} \rightleftharpoons \mathrm{Tris} + \mathrm{H^+}$$

26.8 mL 0.2 M HCl ⇒ strong acid, completely dissociates
+ 50.0 mL 0.2 M Tris ⇒ weak acid/base buffer
bring to total volume of 200 mL
pKa at 20°C = 8.3 $K_a = 10^{-8.3}$

a) What is the resulting pH (at 20°C)?
Easiest ⇒
use Henderson-Hasselbach

$$pH = pK_a + \log\frac{[\mathrm{Tris}]}{[\mathrm{TrisH^+}]}$$

~~[illegible]~~ = ~~[illegible]~~

HCl release how many moles H^+?
$(26.8 \times 10^{-3} L)(0.2 \text{ mol } L^{-1}) = 5.36 \times 10^{-3}$ mole
How many moles initial Tris? (neutral)
$(50 \times 10^{-3} L)(0.2 \text{ mol } L^{-1}) = 10 \times 10^{-3}$ mole

Strong acid → Now 5.36×10^{-3} mol Tris·H⁺ // $(10-5.36) \times 10^{-3}$ mol Tris

$$pH = 8.3 + \log \frac{\frac{4.64 \times 10^{-3}\ mol}{0.2\ L} = 23.2\ mM}{\frac{5.36 \times 10^{-3}\ mol}{0.2\ L} = 26.8\ mM}$$

$$= 8.3 + \log \frac{4.64}{5.36} = 8.2$$

b) Buffer capacity ⇒ **important Concept**

(Distilled water, pH 2 ⇒ Bad?) ⇐ Story

Define buffer capacity: $\frac{\Delta pH}{\Delta \text{ mole } H^+ \text{ (or } OH^-)}$

If we add 1.0 mL of 1.0 M HCl, what happens?

$\#$ moles HCl $= (10^{-3}\ L)(1.0\ mol\ L^{-1}) = 10^{-3}$ moles

Ignore volume change (200 → 201 mLs)

Book goes to 1 Liter total volume here. Let's keep it this way

$$pH = 8.3 + \log \frac{\left(\frac{(4.64-1.0)\times 10^{-3}\ mol}{.2\ L}\right)}{\frac{(5.36+1.0)(\times 10^{-3}\ mol)}{0.2\ L}}$$

$$= 8.3 + \log \frac{3.64}{6.36} = 8.06$$ Relatively small change

* Buffer capacity depends on [Buffer], pKa, pH initial

Temperature-dependence of K

$$\frac{\Delta pK_a}{\Delta T} = \frac{-0.029}{1\ K} \quad \text{(FOR TRIS)}$$

Thus if we go from 20° → 37°C $\Delta T = 17K$

the ΔpK_a $(-0.029\ K^{-1})(17K) = -0.49$

$$pK_a^{37^\circ} = 8.3 - 0.49 = 7.8$$

From above

$\therefore$ $pH = 7.8 + \log \frac{4.64}{5.36} = 7.7$

(very different from 8.2)

T ⇒ 20° → 37°
pH ⇒ 8.2 → 7.7   Big Drop.

Similarly   T ⇒ 20° → 4°C (ice bath)

$$\Delta pK_a = (-0.029\ K^{-1})(-16\ K) = +0.464$$

$$pH = 8.76 + \log \frac{4.64}{5.36} = 8.7$$

So if you pH buffer at RT, and then use it at 4°C or 37°C, the *real* pH will be off by ± ≈ 0.5 pH units

Could be substantial!