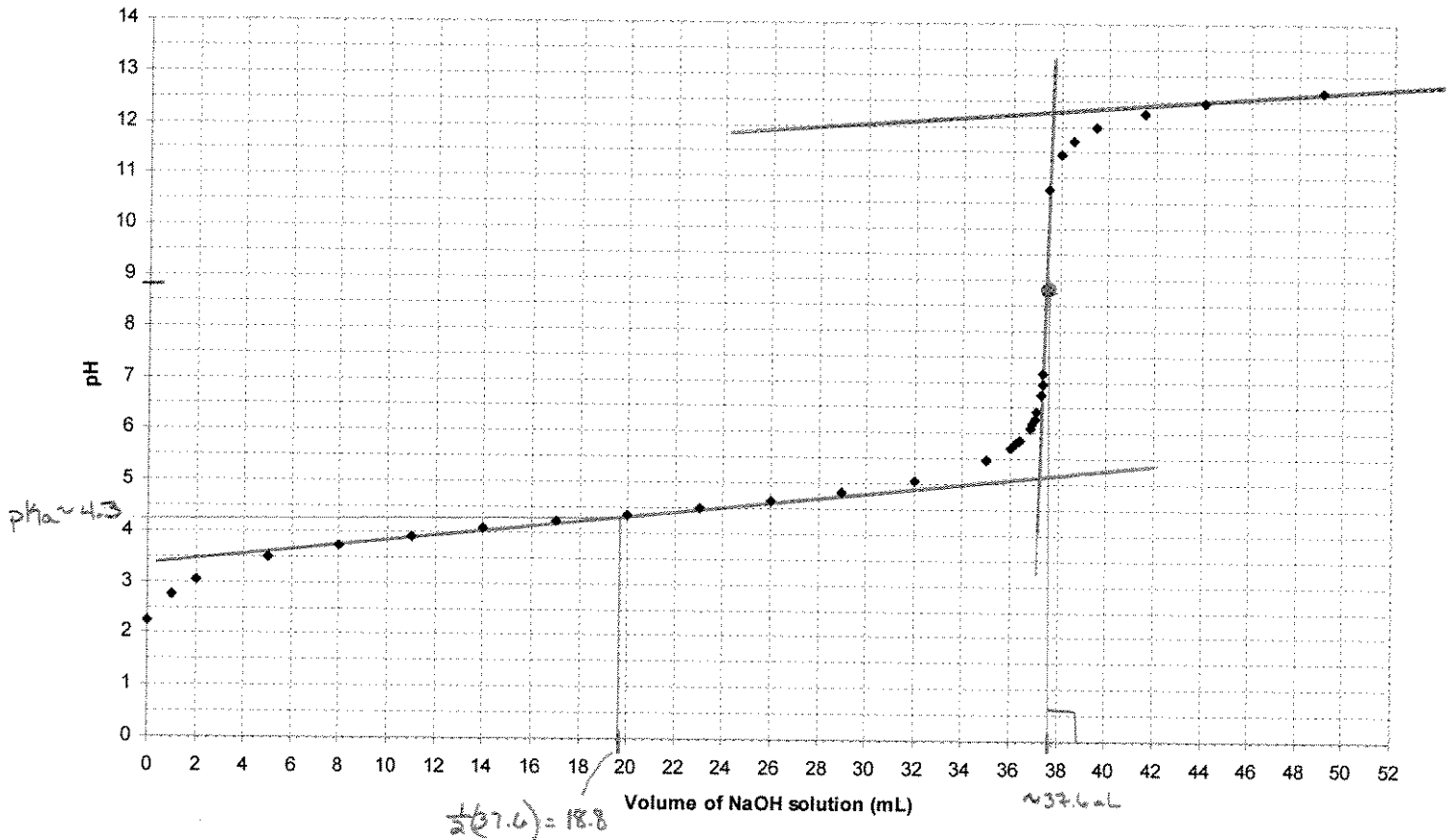




2. (20 points) A 15.0-mL sample of an unknown *monoprotic* acid (HA) of unknown concentration was titrated using standardized 0.250 M NaOH solution. The pH was monitored during the titration, and the following titration data was collected.

pH Analysis of a Weak Acid / Strong Base titration



Draw in the appropriate curve. After making an appropriate graphical analysis of the equivalence point, answer the following questions:

A) What is the pH at equivalence?

④  $\boxed{pH = 8.8}$

B) What is the concentration of the unknown acid?

⑧ 
$$\frac{37.6 \text{ mL NaOH} \mid 0.25 \text{ mol NaOH} \mid 1 \text{ mol HA}}{1000 \text{ mL} \mid 1 \text{ mol NaOH}} = 0.0094 \text{ mol HA}$$

$$[HA] = \frac{0.0094 \text{ mol}}{0.015 \text{ L}} = \boxed{0.63 \text{ M}}$$

C) What is the  $pK_a$  of the unknown acid?

⑤  $\boxed{pK_a \approx 4.3}$

D) What is the  $K_a$  of the unknown acid?

③  $\boxed{K_a = 10^{-4.3} = 5 \times 10^{-5}}$

3. (15 points) A buffer is prepared by mixing 25.0 mL of a 0.200 M sodium acetate ( $\text{CH}_3\text{COONa}$ ) solution and 15.0 mL of 0.200 M acetic acid ( $\text{CH}_3\text{COOH}$ ).

Acetic acid:  $K_a = 1.8 \times 10^{-5}$ .

Henderson-Hasselbalch equation:  $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$

$\text{p}K_a = 4.74$

A) What is the pH of the buffer?

⑤  $\text{pH} = 4.74 + \log\left(\frac{25}{15}\right)$

$\text{pH} = 4.96$

B) Can the buffer consume more moles of strong acid (SA), strong base (SB), or equal amounts of SA or SB before the buffer capacity is exceeded? Explain briefly.

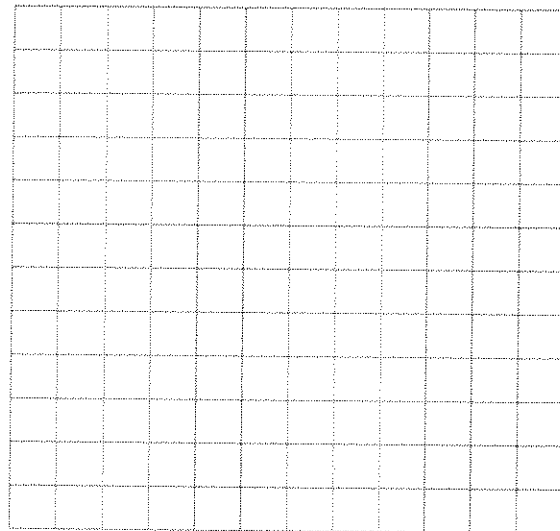
④ More moles of SA, as there is more of the conjugate base available than the conj. acid of the HOAc / NaOAc pair.

C) Indicate the influence (INCREASE, DECREASE, NO CHANGE) on the pH of the solution with the addition of each of the following to the buffer solution (assume buffer capacity is not exceeded).

- ① i. 1.0 mL of 1.0 M NaOH Increase ↑
- ① ii. 1.0 mL of 1.0 M HCl Decrease ↓
- ② iii. 10.0 mL of carbonate-free DI water NO CHANGE
- ① iv. 5.0 mL of 0.50 M  $\text{CH}_3\text{COOH}$  Decrease ↓
- ① v. 5.0 mL of 0.50 M  $\text{CH}_3\text{COONa}$  Increase ↑

4. (20 points) The following  $K_{sp}$  data was collected for the dissolution of the salt, vanadium (III) phosphate:  $VPO_4$ .  
 (Note: Actual graphing of the data is NOT required and will NOT be graded. All of the points very closely fit a line. The grid is provided only if you find graphing helpful in answering the question.)

Temp. (°C)	$K_{sp}$	Temp (K)	$\frac{1}{T}$	$\ln K$
* 85	14 700	358	0.00279	9.60
63	1 040	336	0.00298	6.95
44	79.0	317	0.00315	4.37
* 25	4.34	298	0.00336	1.47
3.0	0.093	276	0.00362	-2.38



The relationship of  $K$  to temperature is:

$$\ln K = -\frac{\Delta H}{R} \left( \frac{1}{T} \right) + \frac{\Delta S}{R}$$

Some of the following relationships may also be useful in answering this question:

Slope is defined as  $m = \frac{\Delta y}{\Delta x}$

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

You may assume  $\Delta H$  and  $\Delta S$  do not change over the temperature range of this experiment. Therefore,  $\Delta H = \Delta H^\circ$  and  $\Delta S = \Delta S^\circ$ .

Based on the data provided,

- A) Calculate  $\Delta H$  for the reaction.

$$\text{slope} = \frac{\Delta(\ln K)}{\Delta\left(\frac{1}{T}\right)} = \frac{9.60 - 1.47}{0.00279 - 0.00336} = \frac{8.13}{-5.7 \times 10^{-4}} = -14263$$

⑩ 
$$\frac{-\Delta H}{R} = -14,263 \Rightarrow \Delta H = (14263)(8.314) = \boxed{119 \text{ kJ/mol}}$$

- B) Calculate  $\Delta G^\circ$  for the reaction.

⑤ 
$$\Delta G^\circ = -RT \ln K = -(8.314)(298) \ln(4.34) = -3640 \text{ J/mol}$$
  

$$\boxed{\Delta G^\circ = -3.6 \text{ kJ}}$$

- C) Calculate  $\Delta S$  for the reaction.

⑤ 
$$\Delta S^\circ = \frac{\Delta G^\circ - \Delta H^\circ}{-T} = \frac{-3640 \text{ J/mol} - 119,000 \text{ J/mol}}{-298 \text{ K}} = \boxed{410 \text{ J/K}\cdot\text{mol}}$$