

5 questions + extra credit problem, 8 pages.

Answer on these sheets only. Additional space on last page.

If you need extra sheets, please ask your proctor or TA.

If you continue a problem on an additional page, please indicate that on the original problem page.

Note: Only these papers can be used; no other notes are allowed.

Please answer each question concisely. Show your calculations.

You may (and in some cases, must) draw explanatory diagrams.

Label all axes and features on graphs and diagrams.

You may not use a calculator, computer, watch, smart device, or electronics of any sort.

Irrelevant and/or incorrect material will result in loss of points.

→ Only exam answers in pen will be considered for regrading.

Table of constants and conversions

Speed of light: $c = 3 \times 10^8$ m/s

Faraday constant = 96500 coul/mole

Electron charge magnitude: $e = 1.6 \times 10^{-19}$ C

Plank's constant: $\hbar = 1.1 \times 10^{-34}$ J-s

Gas constant: $R = 0.08206$ L-atm/mol-K = 8.314 J/mol-K = 1.987 cal/mol-K

Boltzmann constant: $k_B = 1.4 \times 10^{-23}$ J/K

Electron rest mass: $m = 9.1 \times 10^{-31}$ kg

Proton rest mass: $M = 1.7 \times 10^{-27}$ kg

1 mole = 6.02×10^{23}

TOTAL = 93 (11)
 1) 15
 2) 15
 3) 29
 4) 18
 5) 15
 EC) 1

arbitrary
 fl
 unit
 wave length

Midterm 1

Energy Conversion Table

	eV	cm ⁻¹	kcal/mol	kJ/mol	K	J	Hz
eV	1	8 065.73	23.060 9	96.486 9	11 604.9	1.602×10^{-19}	$2.418 04 \times 10^{14}$
cm ⁻¹	$1.239 81 \times 10^{-4}$	1	0.002 859 11	0.011 962 7	1.428 79	$1.986 30 \times 10^{-23}$	$2.997 93 \times 10^{10}$
kcal/mol	0.043 363 4	349.757	1	4.18400	503.228	6.95×10^{-21}	$1.048 54 \times 10^{13}$
kJ/mol	0.010 364 10	83.593	0.239001	1	120.274	1.66×10^{-21}	$2.506 07 \times 10^{12}$
K	0.000 086 170 5	0.695 028	0.001 987 17	0.008 314 35	1	$1.380 54 \times 10^{-23}$	$2.083 64 \times 10^{10}$
J	$6.241 81 \times 10^{18}$	$5.034 45 \times 10^{22}$	1.44×10^{20}	6.02×10^{20}	$7.243 54 \times 10^{22}$	1	$1.509 30 \times 10^{33}$
Hz	$4.135 58 \times 10^{-15}$	$3.335 65 \times 10^{-11}$	$9.537 02 \times 10^{-14}$		$4.799 30 \times 10^{-11}$	$6.625 61 \times 10^{-34}$	1

$\Delta G^\circ = -nFE^\circ = -2.303 RT \log_{10} K_{eq}$

$pH = pK_a - \log_{10} ([HA]/[A^-])$

You will find a periodic table for your reference on the next page.

$p \rightarrow n + e^+$

$n \rightarrow p + e^-$

B

Question 1 (15 points):

1) Radioactive ^{18}F is used in many biochemical studies and has a half-life of ~ 100 min. There is only one stable isotope of fluorine (which you can determine from the attached periodic table). The ^{18}F is often put in place of a $-\text{OH}$ (hydroxyl) group in biomolecules and that molecule is similar enough to be useful in tracking where the original biomolecule would be found *in vivo*.

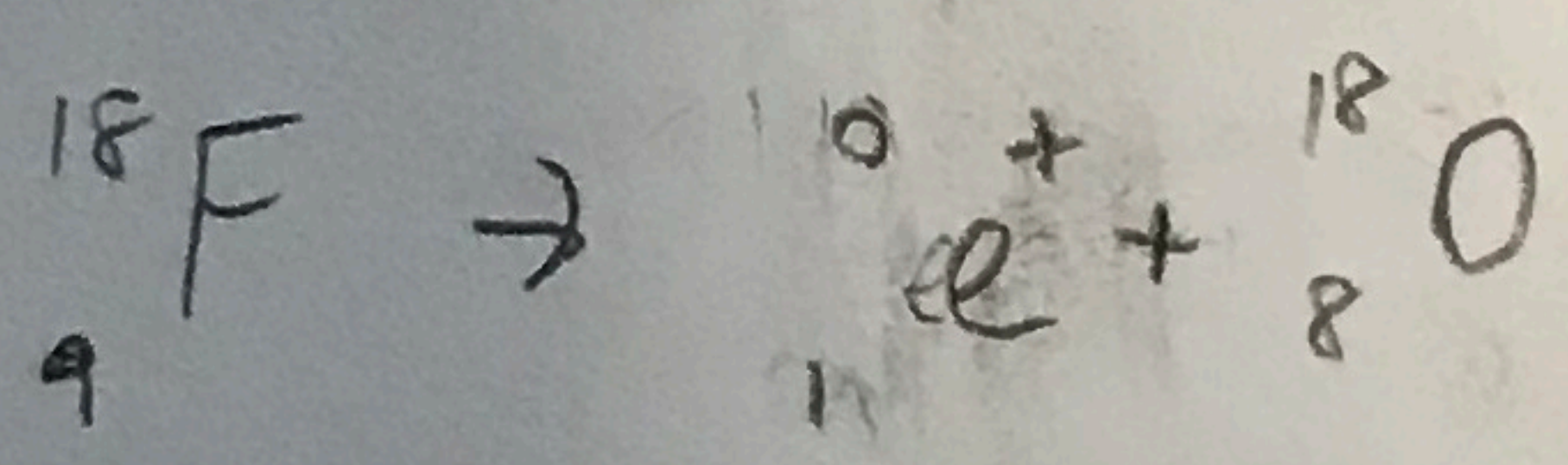
a) What is the most likely decay pathway for ^{18}F ? Concisely explain your reasoning.

Write a balanced reaction for this decay. (10 points)

on deficient
positron emission
or
electron capture
elements

make sure numbers
add up (partial
credit)

"F" normally is ^{19}F , so ^{18}F is missing one neutron, meaning that it is neutron deficient.



The most stable form of F is

^{19}F which is seen by its mass on

the periodic table as 18.998. The radioactive substance is therefore neutron deficient so it will therefore want to increase its number of neutrons to reach a more stable proton to neutron ratio through a positron emission.

F is also the most electronegative element

b) After 5 hours, what fraction of the original ^{18}F remains? (5 points)

$$\frac{5 \text{ hours}}{1 \text{ hour}} \times \frac{100 \text{ minutes}}{1 \text{ hour}} = 300 \text{ minutes}$$

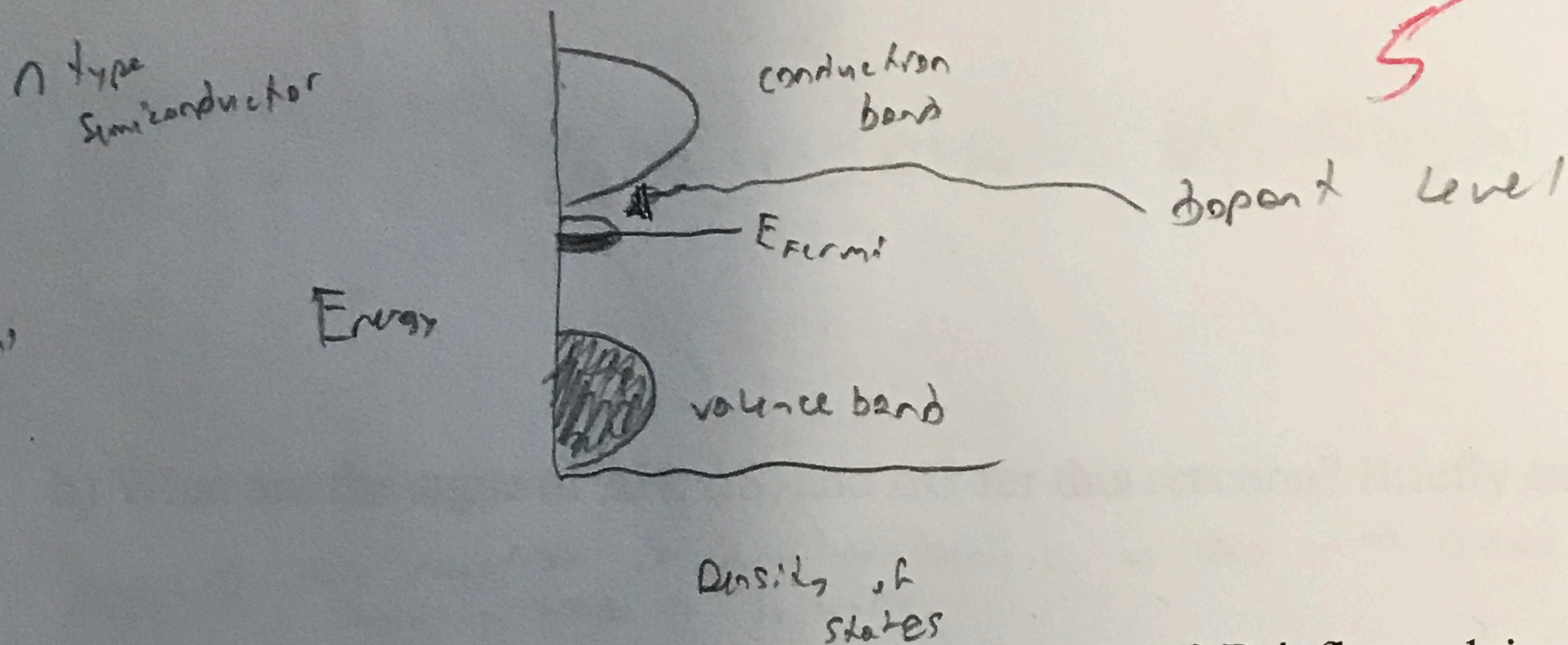
$$\text{half life} = \frac{300}{100} = 3$$

goes through 3 half
lives

$$\left(\frac{1}{2}\right)^3 = \left(\frac{1}{2}\right)^3 = \frac{1}{8} \text{ of original amount will remain after 5 hours}$$

Question 2 (15 points):

2) a) Draw an energy level diagram for an *n*-type semiconductor. Identify the bands (including which are filled), the Fermi energy, and the dopant level. (5 points)



The dopant level is closer to the conduction band in an *n*-type semiconductor

b) How does conductivity change with temperature? Briefly explain why. (5 points)

carriers become thermally excited

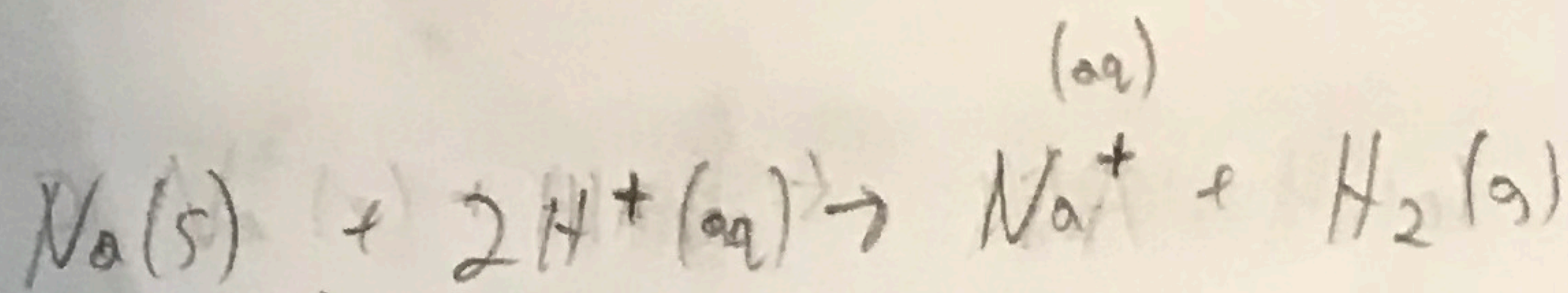
In a semiconductor, an increase in temperature will increase the conductivity because the charge carriers will become thermally excited.

c) How does the conductivity of a metal change with temperature? (5 points)

In a metal, an increase in temperature will decrease conductivity.

Question 3 (30 points):

3)a) Write the balanced reaction for what happens when we put sodium, Na(s), in acidic aqueous solution. (5 points)



b) What are the signs of ΔH , ΔS , and ΔG for this reaction? Briefly explain why. (10 points)

$\Delta H < 0$ this reaction is very exothermic as seen with release of heat/fire
breaking bonds is favorable

$\Delta S > 0$ more moles of gas are being formed which is entropically favorable

$\Delta G < 0$ This reaction is spontaneous due to the signs of ΔH and ΔS as well as by chemical intuition

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

c) What happens to the temperature and pH of the water in this reaction? Briefly explain why. (5 points)

The temperature of the water will greatly increase due to the exothermic reaction that releases heat. The pH will increase and become less acidic because the H^+ (hydronium ions) in solution react to become a gas. The decrease in H^+ concentration makes the water less acidic.

d) If we ran the reaction as an electrochemical cell, what would the sign of the standard cell potential, E° , be? Briefly explain why. (5 points)

$$\Delta G = -nFE^\circ$$

This reaction is favorable meaning the $\Delta G < 0$ so therefore the sign of $E^\circ > 0$ (positive) in order to keep ΔG negative.

e) Write the balanced reduction and oxidation half-cell reactions for (d). What are the signs of the standard half-cell potentials (as the reactions are written above)? (5 points)

oxidation

$$2\text{Na} \rightarrow 2\text{Na}^+ + 2e^- \quad \Delta E > 0 \text{ oxidation}$$

reduction

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad \Delta E > 0 \text{ reduction}$$

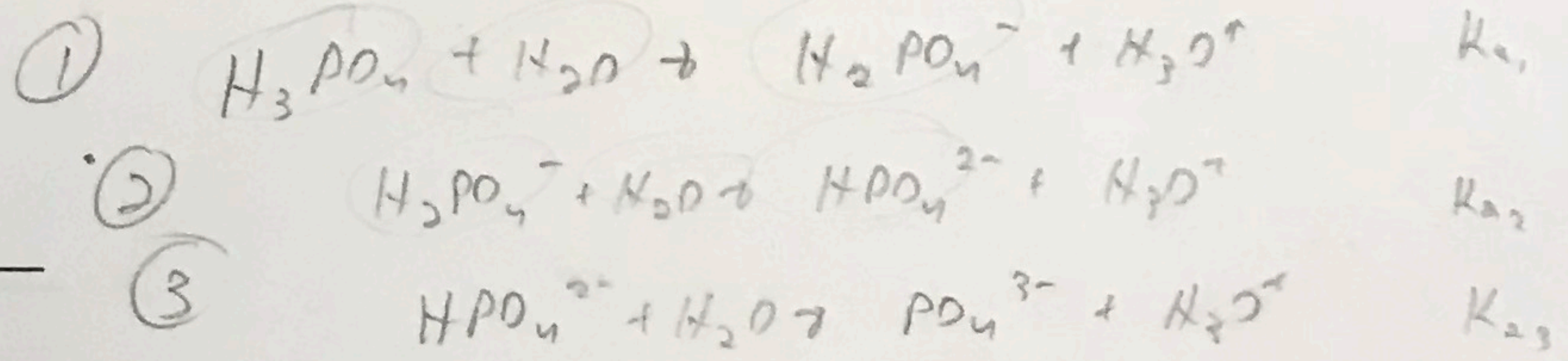
Na has a very low ionization energy and therefore has a positive oxidation potential

The hydrogen is being reduced which is favorable meaning a positive reduction potential

$\Delta E^\circ > 0$

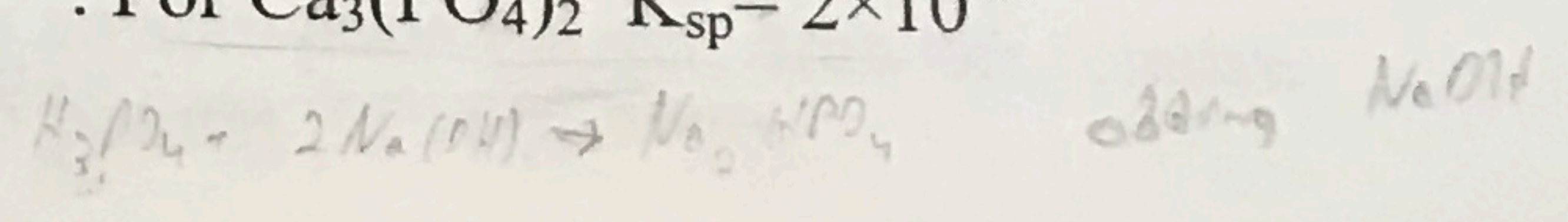
5

29



Question 4 (20 points):

4) For H_3PO_4 : $K_{a1} = 7 \times 10^{-3}$, $K_{a2} = 6 \times 10^{-8}$, and $K_{a3} = 4 \times 10^{-13}$. For $Ca_3(PO_4)_2$ $K_{sp} = 2 \times 10^{-29}$
 Starting with a 0.01 M aqueous solution of Na_2HPO_4 :



a) Name all the chemical species in solution (ions and neutrals). (10 points)

There are 2 Na^+ ions

all of Na_2HPO_4 is also in H_2O 9

$H_2PO_4^-$, H_2O , H_3O^+ , HPO_4^{2-} , OH^- , PO_4^{3-} , H_3PO_4

b) Is the solution acidic, basic, or neutral? Briefly explain your answer. (5 points)

The solution is acidic because the HPO_4^{2-} can still react with water to increase the amount of H_3O^+ (which is the definition of an Arrhenius acid)
 $K_w = K_a K_b$ 4

$K_{a2} = \frac{(H_3O^+)(HPO_4^{2-})}{(H_2PO_4^-)}$
 HPO_4^{2-} can act as an acid or a base (as it can react with water to create OH^- or H_3O^+ ions) however, based on its K_{a2} value, it is very small therefore its K_b value is larger meaning it will act as a base.

c) 1 M $CaCl_2$ is added until a precipitate forms. Does this change the pH? If so, has it gone up or down? Briefly explain your answer. (5 points)

Na_2HPO_4 (added)

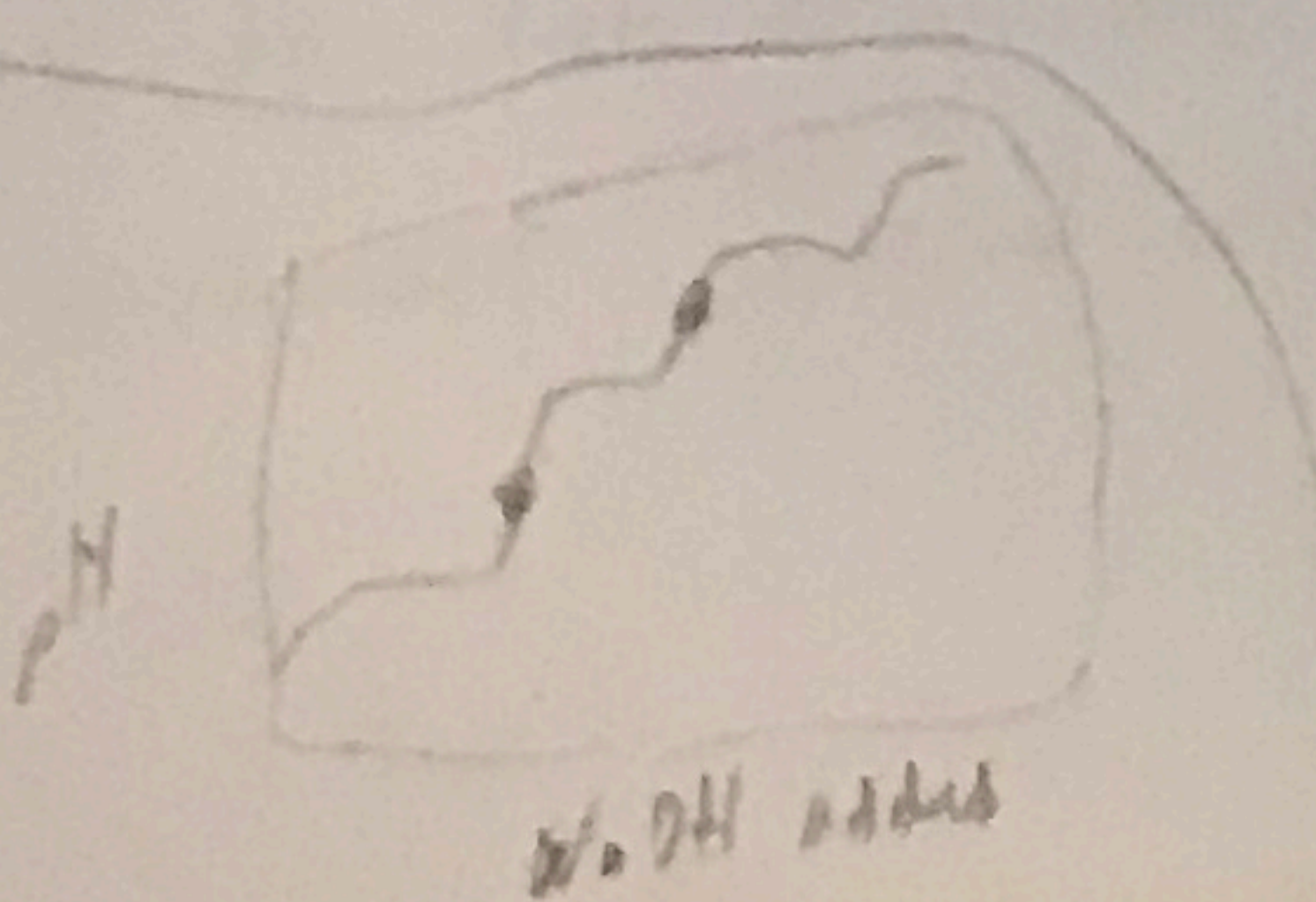
$K_{a2} = \frac{(H_3O^+)(HPO_4^{2-})}{(H_2PO_4^-)}$ 5

yes! this does change the pH; adding $CaCl_2$ will then dissociate into Ca^{2+} and Cl^- ions. As seen by the K_{sp} for $Ca_3(PO_4)_2$, the value is very small meaning that very little of it will dissolve, in fact, most of it will precipitate out. By doing this, most of the PO_4^{3-} ions will be taken out of the solution as a precipitate

$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2$
 small K_{sp} means dissolve very little

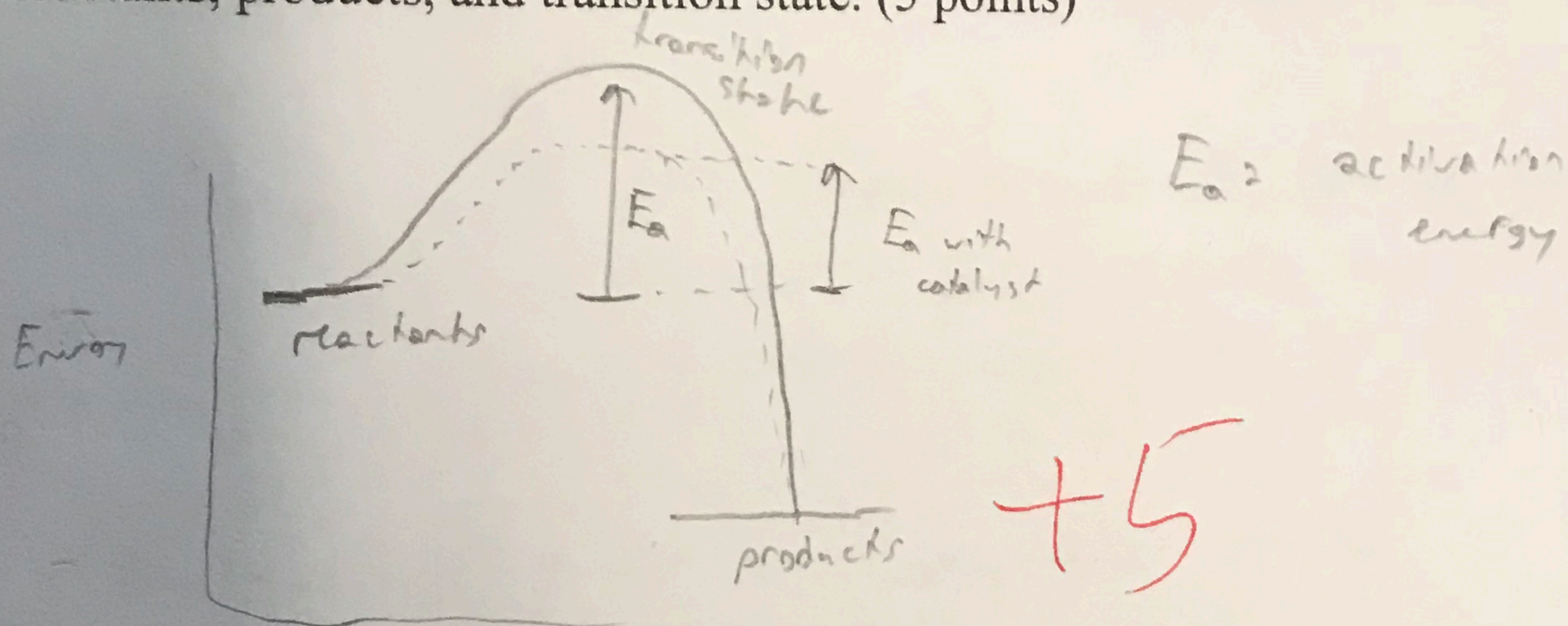
and the H^+ ions will have to increase as a result of the taking up of PO_4^{3-} ions by the addition of $CaCl_2$ so therefore pH will decrease and become more acidic.

Titration curve for triprotic acid



Question 5 (20 points):

5)a) For an exothermic and spontaneous reaction that has an activation barrier, draw the relative energies of the reactants, products, and transition state. (5 points)



b) On the above plot, indicate the effect of adding a catalyst and describe that effect here. (5 points)

The dotted line represents the added catalyst which lowers the activation energy for the reaction.

+5

c) What is the effect of the catalyst on the energies of the reactants and products? (5 points)

Catalysts have no effect on thermodynamics and therefore have no effect on the energies of the reactants or products. It only lowers the activation energy.

+5

d) What is the effect of temperature on the rate of reaction and why? (5 points)

$\Delta H < 0$

The reaction is said to be exothermic so by Le Chatelier's principle, raising the temperature will cause the rate of the reaction to decrease. In order to shift its balance back to equilibrium (once again... Le Chatelier's principle that a disturbed system will move to counter-act that disturbance).

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Extra credit #1 (2 points):

X-rays can be used both for spectroscopy (e.g., fluorescence) and diffraction. What do we learn from each and how are they different?

X-ray Spectroscopy excites core electrons which can be used for elemental identification. In fluorescence, the photon enters with $h\nu$ and then will lose energy due to vibrational states and leave at $h\nu'$. The loss of energy identifies elements.

In X-ray diffraction, the X-rays are going into a crystal which can then tell the bond lengths and distances between substances through the separation observed.

+

Continue any answers below if you need more room.

Continuation of problem # _____