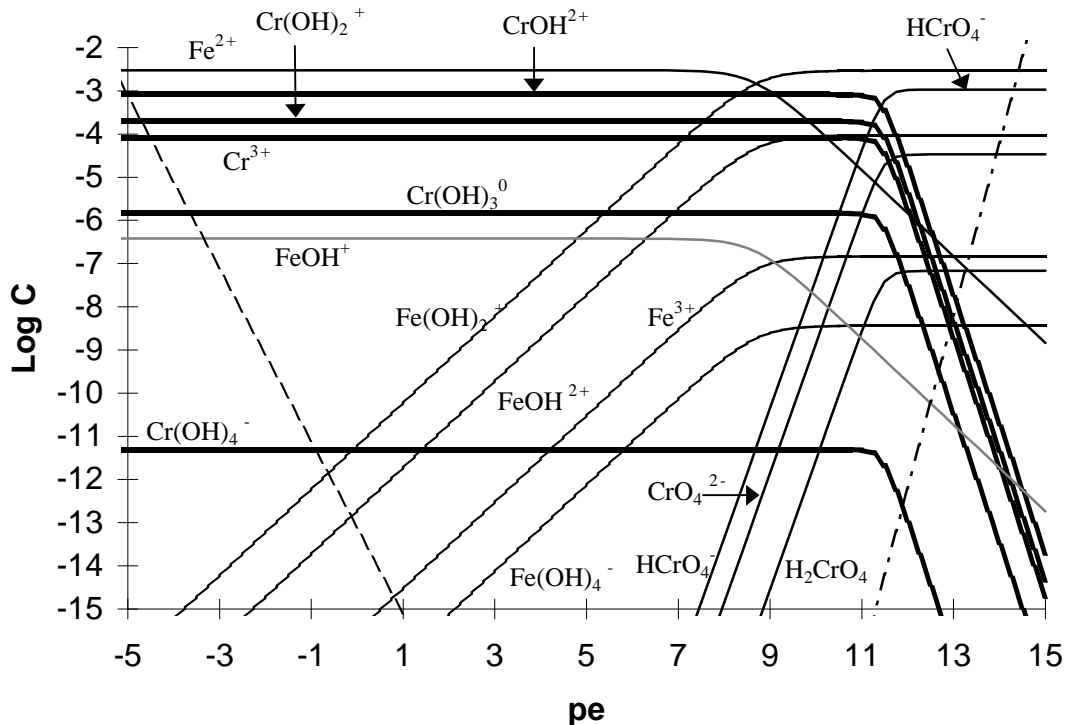
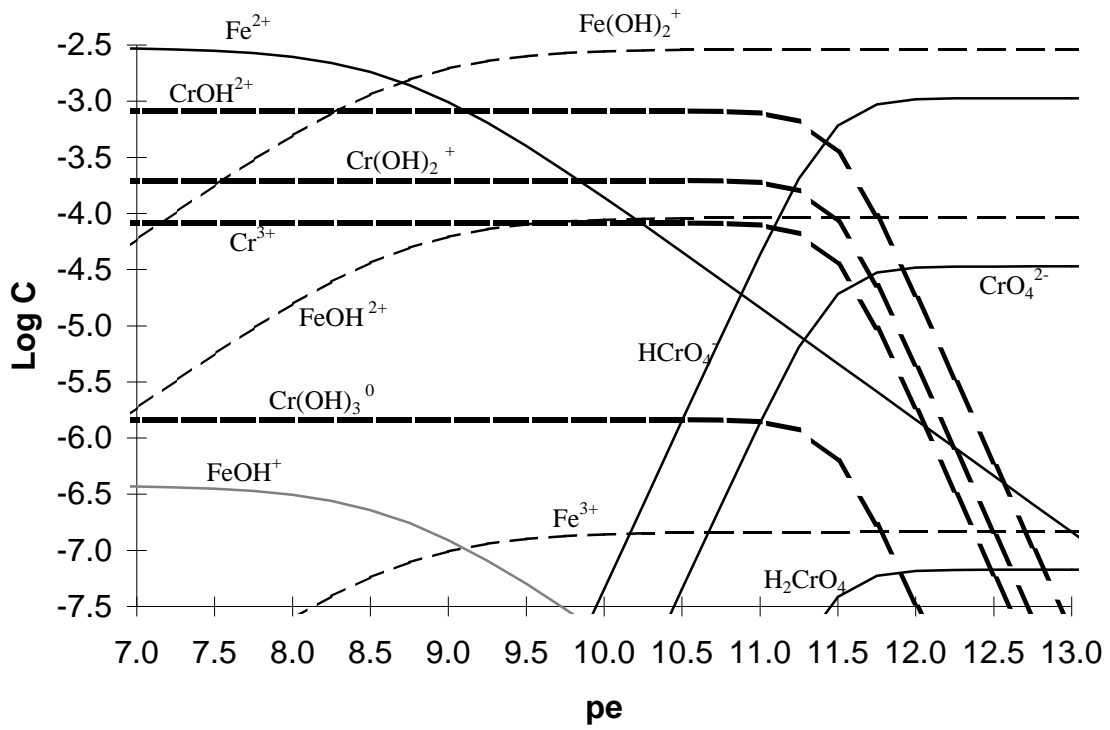


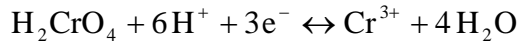
A log C - pe diagram for a pH 5 system containing  $1.1 \times 10^{-3}$  M *TOTCr* and  $3 \times 10^{-3}$  M *TOTFe* is shown below. Based on the information in the diagram, answer the following questions.

- What is  $pe^0$  for the  $H_2CrO_4/Cr^{3+}$  redox couple?
- What is  $pK_{a2}$  for chromic acid ( $H_2CrO_4$ )?
- Write the *TOTe* equation for a system made by adding  $3 \times 10^{-3}$  M  $FeCl_2$  to a solution initially containing  $1.1 \times 10^{-3}$  M Cr(VI) and no Cr(III) at pH 5. Assuming the system is well-buffered at this pH, what are the approximate values of  $pe$  and *TOTCr*(VI) at equilibrium? Consider only redox reactions of the Fe(III)/Fe(II) and Cr(VI)/Cr(III) couples.
- Assuming that Cr(VI) species constitute the only weak acid/base system in the initial solution, how would the addition of the  $FeCl_2$  and the subsequent reactions affect the alkalinity and pH of the solution (increase, decrease, no change)? Explain briefly.





(a) The relevant half-reaction is as follows:



The equilibrium constant for this reaction is:

$$K = \frac{\{\text{Cr}^{3+}\}}{\{\text{H}_2\text{CrO}_4\} \{\text{H}^+\}^6 \{\text{e}^-\}^3}$$

$$\log K = \log \frac{\{\text{Cr}^{3+}\}}{\{\text{H}_2\text{CrO}_4\}} + 6\text{pH} + 3\text{pe}$$

From the graph, we can obtain values for  $\{\text{H}_2\text{CrO}_4\}$  and  $\{\text{Cr}^{3+}\}$  at any arbitrary  $\text{pe}$  and substitute those values (along with the known  $\text{pH}$ ) into the above equation to find  $\log K$  for the reaction of interest. One convenient condition for the evaluation is at  $\text{pe} = 12.5$ , where  $\{\text{H}_2\text{CrO}_4\} = \{\text{Cr}^{3+}\}$ . Substituting these conditions into the equilibrium constant expression, we obtain:

$$\log K = 0 + 6(5.0) + 3(12.5) = 67.5$$

$\text{pe}^\circ$  equals  $\log K$  for the reduction reaction for a one-electron transfer. The above reaction is for a three-electron transfer, so  $\text{pe}^\circ = 67.5/3 = 22.5$ .

(b) The graph indicates that, at the given  $\text{pH}$  of 5.0, the value of  $\{\text{CrO}_4^{2-}\}$  is always 1.5 log units less than that of  $\{\text{HCrO}_4^-\}$ , so the value of  $K_{a2}$  can be found as follows:

$$K_{a2} = \frac{\{\text{H}^+\} \{\text{CrO}_4^{2-}\}}{\{\text{HCrO}_4^-\}} = \frac{\{\text{H}^+\} (10^{-1.5} \{\text{HCrO}_4^-\})}{\{\text{HCrO}_4^-\}} = 10^{-1.5} \{\text{H}^+\}$$

$$\log K_{a2} = -1.5 + \log \{\text{H}^+\} = -6.5$$

(c) The species to be considered include all those shown on the graph. We need to choose a compound in each oxidation state for each element as a component. We can choose these components somewhat arbitrarily, although if we are going to use a  $\log c - \text{pe}$  diagram to determine the equilibrium  $\text{pe}$ , it is most convenient to choose chemicals in the dominant oxidation states. We can identify the dominant oxidation states by imagining the inputs to consist of oxidized species and electrons, and then allocating the electrons sequentially to the available oxidants from strongest to weakest. From the  $\log c - \text{pe}$  diagram, we can see that the dominant oxidation state for Cr changes from +VI to +III at  $\text{pe} \sim 11.4$ , and that for Fe changes from +III to +II at  $\text{pe} \sim 8.9$ . Based on these values, the dominant oxidation states at equilibrium are expected to be Cr(+III) and Fe(+III), as shown in the following table.

Oxidized/ Reduced	$pe_{pH}$	$TOTi$	Fraction Reduced	$e^-$ Remaining
Cr(VI)/Cr(III)	11.4	$1.1 \times 10^{-3}$	0%	$3.0 \times 10^{-3}$
			91%	0
Fe(III)/Fe(II)	8.9	$1.0 \times 10^{-3}$	0%	0

The tableau for deriving the  $TOTe$  equation using Cr(III) and Fe(III) as components is shown below. Because we only need to know the values in the  $e^-$  column to write the  $TOTe$  equation, the tableau can be condensed by including all the species containing Cr or Fe in a given oxidation state in a single row.

	H <sub>2</sub> O	H <sup>+</sup>	$e^-$	Fe(III)	Cr(III)	Conc'n
H <sub>2</sub> O	1	0	0	0	0	
H <sup>+</sup>	0	1	0	0	0	
$e^-$	0	0	1	0	0	
Fe(III)	0	var	0	1	0	
Fe(II)	0	var	1	1	0	
Cr(VI)	0	var	0	0	0	
Cr(III)	1	0	3	0	1	
<b>Inputs</b>						
FeCl <sub>2</sub>	0	var	1	1	0	$3.0 \times 10^{-3}$
NaHCrO <sub>4</sub>	0	var	-3	0	1	$1.1 \times 10^{-3}$

The  $TOTe$  is a mass-based equation, but assuming that the solution behaves ideally, so that the activities of dissolved species can be equated with their molar concentrations, it can be written as follows:

$$TOTe_{in} = TOTe_{eq}$$

$$(3 \times 10^{-3}) - 3(1.1 \times 10^{-3}) = \sum(\text{Fe(II)}) - 3\sum(\text{Cr(VI)})$$

$$3\sum(\text{Cr(VI)}) = \sum(\text{Fe(II)}) + 3 \times 10^{-4}$$

The equation is satisfied at approximately  $pe = 11.1$  (Figure 3). At this  $pe$ ,  $TOTCr(VI)$  is approximately  $1 \times 10^{-4} M$  and  $TOTFe(II)$  is approximately  $10^{-5}$ , i.e., about 99% of the  $Fe(II)$  has been oxidized, reducing most of the  $Cr(VI)$ . Since the  $Fe(II)$  dose was less than the stoichiometric amount required to reduce all the  $Cr$ , some hexavalent  $Cr$  remains.

