Another example of a redox titration.

50.00 mL of 0.0100 M Fe^{2+} in 0.1 M H_2SO_4 is titrated with 0.0100 M Ce^{4+}

a) What is the reaction when Ce^{4+} is added to Fe^{2+}?

$Fe^{2+} = Fe^{3+} + e^-$ $E^0 = 0.771$ V

$Ce^{4+} + e^- = Ce^{3+}$ $E^0 = 1.61$ V

$$E^0_{cell} = E_{cath} - E_{anod} = 1.61\text{ V} - 0.771\text{ V} = 0.839\text{ V}$$

So the rxn is spontaneous.

$$Ce^{4+} + Fe^{2+} = Fe^{3+} + Ce^{3+}$$

b) Calculate E_{cell} with SCE and Pt at 25.00 mL titrant added.
c) 50.00 mL added
d) 75.00 mL added

b) 25.00 mL of 0.0100 M Ce^{4+}

Initial mol Fe^{2+} = 50.00 mL(0.0100 M) = 0.500 mmol

Added mol Ce^{4+} = 25.00 mL(0.0100 M) = 0.250 mmol

Ce^{4+}	+ Fe^{2+}	= Fe^{3+}	+ Ce^{3+}
0.250	0.500 mmol	0	0
-0.250	-0.250	+0.250	+0.250 mmol
0	0.250	0.250	0.250 mmol

$Fe^{2+/3+}$ governs the potential at the Pt wire.

Total vol = 50.00 + 25.00 mL

$[Fe^{2+}]$ = 0.250 mmol / 75.00 mL = 3.33e-3 M

$[Fe^{3+}]$ = 0.250 mmol / 75.00 mL = 3.33e-3 M

$E = 0.771 - 0.0592 \log [Fe^{2+}] / [Fe^{3+}] = 0.771V$

$E_{cell} = 0.771 - 0.241 = 0.530$ V

c) 50.00 mL of 0.0100 M Ce^{4+}

Added mol Ce^{4+} = 50.00 mL(0.0100 M) = 0.500 mmol

This is the Eq. Pt.

At Eq. Pt. $[Ce^{4+}] = [Fe^{2+}]$ & $[Fe^{3+}] = [Ce^{3+}]$

2 Nernst Eqn.

$$E = 0.771 - 0.0592 \log [Fe^{2+}] / [Fe^{3+}]$$
$$\underline{+E = 1.61 - 0.0592 \log [Ce^{3+}] / [Ce^{4+}]}$$
$$2E = 2.381 - 0.0592 \log [Fe^{2+}] / [Fe^{3+}] - 0.0592 \log [Ce^{3+}] / [Ce^{4+}]$$

$$2E = 2.381 - 0.0592 \log [Fe^{2+}][Ce^{3+}] / [Fe^{3+}][Ce^{4+}]$$

Sub $2E = 2.381 - 0.0592 \log [Fe^{2+}] [Fe^{3+}] / [Fe^{3+}][Fe^{2+}]$

$$E = 1.19$$

$$Ecell = 1.19 - 0.241 = 0.95 \text{ V}$$

c) 75.00 mL of 0.0100 M Ce^{4+}

Added mol Ce^{4+} = 75.00 mL(0.0100 M) = 0.750 mmol

Ce^{4+}	+ Fe^{2+}	= Fe^{3+}	+ Ce^{3+}
0.750	0.500 mmol	0	0
-0.500	-0.500	+0.500	+0.500 mmol
0.250	0	0.500	0.500 mmol

$[Ce^{4+}]$ = 0.500 mmol / 125.0 mL = 4.00e-4 M
$[Ce^{3+}]$ = 0.250 mmol / 125.0 mL = 2.00e-4 M

$E = 1.61 - 0.0592 \log [Ce^{3+}] / [Ce^{4+}] = 1.61 - 0.0592 \log 2.00\text{e-}4 / 4.00\text{e-}4$

$E = 1.63\ V$

$E_{cell} = 1.63 - 0.241\ V = 1.39\ V$