Chapter 8: *Applications of Aqueous Equilibria*
Chapter 10: *Spontaneity, Entropy, and Free Energy*

Chapter 8: #45, 47, 53, 54, 55, 71, 123, 131

Acid Base Titrations

45. This is a strong acid ($HClO_4$) titrated by a strong base (KOH). Added OH^- from the strong base will react completely with the H^+ present from the strong acid to produce H_2O.

a. Only strong acid present. $[H^+] = 0.200\ M$; pH = 0.699

b. mmol OH^- added $= 10.0\ mL \times \frac{0.100\ mmol\ OH^-}{mL} = 1.00\ mmol\ OH^-$

mmol H^+ present $= 40.0\ mL \times \frac{0.200\ mmol\ H^+}{mL} = 8.0\ mmol\ H^+$

Note: The units mmoles are usually easier numbers to work with. The units for molarity are moles/L but are also equal to mmoles/mL.

	H^+	+	OH^-	→	H_2O	
Before	8.00 mmol		1.00 mmol			
Change	-1.00 mmol		-1.00 mmol			Reacts completely
After	7.00 mmol		0			

The excess H^+ determines the pH. $[H^+]_{excess} = \frac{7.00\ mmol\ H^+}{40.0\ mL + 10.0\ mL} = 0.140\ M$; pH = 0.854

c. mmol OH^- added $= 40.0\ mL \times 0.100\ M = 4.00\ mmol\ OH^-$

	H^+	+	OH^-	→	H_2O
Before	8.00 mmol		4.00 mmol		
After	4.00 mmol		0		

$[H^+]_{excess} = \frac{4.00\ mmol}{(40.0 + 40.0)\ mL} = 0.0500\ M$; pH = 1.301

d. mmol OH^- added $= 80.0\ mL \times 0.100\ M = 8.00\ mmol\ OH^-$; This is the equivalence point since we have added just enough OH^- to react with all the acid present. For a strong acid-strong base titration, pH = 7.00 at the equivalence point since only neutral species are present (K^+, ClO_4^-, H_2O).

e. mmol OH^- added $= 100.0\ mL \times 0.100\ M = 10.0\ mmol\ OH^-$

	H^+	+	OH^-	→	H_2O
Before	8.00 mmol		10.0 mmol		
After	0		2.0 mmol		

Past the equivalence point, the pH is determined by the excess OH^- present.

$[OH^-]_{excess} = \frac{2.0\ mmol}{(40.0 + 100.0)\ mL} = 0.014\ M$; pOH = 1.85; pH = 12.15

47. This is a weak acid ($HC_2H_3O_2$) titrated by a strong base (KOH).

a. Only weak acid is present. Solving the weak acid problem:

	$HC_2H_3O_2$	$\rightleftharpoons$	H^+	+	$C_2H_3O_2^-$
Initial	0.200 *M*		~0		0
	x mol/L $HC_2H_3O_2$ dissociates to reach equilibrium				
Change	$-x$	→	$+x$		$+x$
Equil.	$0.200 - x$		x		x

$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.200 - x} = \frac{x^2}{0.200}, \quad x = [H^+] = 1.9 \times 10^{-3}\ M$$

pH = 2.72; Assumptions good.

b. The added OH^- will react completely with the best acid present, $HC_2H_3O_2$.

$$\text{mmol } HC_2H_3O_2 \text{ present} = 100.0 \text{ mL} \times \frac{0.200 \text{ mmol } HC_2H_3O_2}{\text{mL}} = 20.0 \text{ mmol } HC_2H_3O_2$$

$$\text{mmol } OH^- \text{ added} = 50.0 \text{ mL} \times \frac{0.100 \text{ mmol } OH^-}{\text{mL}} = 5.00 \text{ mmol } OH^-$$

	$HC_2H_3O_2$	+	OH^-	→	$C_2H_3O_2^-$ + H_2O	
Before	20.0 mmol		5.00 mmol		0	
Change	-5.00 mmol		-5.00 mmol	→	+5.00 mmol	Reacts completely
After	15.0 mmol		0		5.00 mmol	

After reaction of all the strong base, we have a buffer solution containing a weak acid ($HC_2H_3O_2$) and its conjugate base ($C_2H_3O_2^-$). We will use the Henderson-Hasselbalch equation to solve for the pH.

$$pH = pK_a + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = -\log(1.8 \times 10^{-5}) + \log\left(\frac{5.00 \text{ mmol}/V_T}{15.0 \text{ mmol}/V_T}\right)$$ where V_T = total volume

$$pH = 4.74 + \log\left(\frac{5.00}{15.0}\right) = 4.74 + (-0.477) = 4.26$$

Note that the total volume cancels in the Henderson-Hasselbalch equation. For the [base]/[acid] term, the mole ratio equals the concentration ratio since the components of the buffer are always in the same volume of solution.

c. mmol OH^- added = 100.0 mL × 0.100 mmol OH^-/mL = 10.0 mmol OH^-; The same amount (20.0 mmol) of $HC_2H_3O_2$ is present as before (it never changes). As before, let the OH^- react to completion, then see what is remaining in solution after this reaction.

	$HC_2H_3O_2$	+	OH^-	→	$C_2H_3O_2^-$ + H_2O
Before	20.0 mmol		10.0 mmol		0
After	10.0 mmol		0		10.0 mmol

A buffer solution results after reaction. Since $[C_2H_3O_2^-] = [HC_2H_3O_2]$ = 10.0 mmol/total volume, then $pH = pK_a$. This is always true at the halfway point to equivalence for a weak acid/strong base titration, $pH = pK_a$.

$$pH = -\log(1.8 \times 10^{-5}) = 4.74$$

d. mmol OH^- added = 150.0 mL × 0.100 *M* = 15.0 mmol OH^-. Added OH^- reacts completely with the weak acid.

	$HC_2H_3O_2$	+	OH^-	→	$C_2H_3O_2^-$ + H_2O
Before	20.0 mmol		15.0 mmol		0
After	5.0 mmol		0		15.0 mmol

We have a buffer solution after all the OH^- reacts to completion. Using the Henderson-Hasselbalch equation:

$$pH = 4.74 + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 4.74 + \log\left(\frac{15.0 \text{ mmol}}{5.0 \text{ mmol}}\right)$$ (Total volume cancels, so we can use mol ratios.)

$pH = 4.74 + 0.48 = 5.22$

e. mmol OH^- added = 200.00 mL × 0.100 *M* = 20.0 mmol OH^-; As before, let the added OH^- react to completion with the weak acid, then see what is in solution after this reaction.

	$HC_2H_3O_2$	+	OH^-	→	$C_2H_3O_2^-$ + H_2O
Before	20.0 mmol		20.0 mmol		0
After	0		0		20.0 mmol

This is the equivalence point. Enough OH^- has been added to exactly neutralize all the weak acid present initially. All that remains that affects the pH at the equivalence point is the conjugate base of the weak acid, $C_2H_3O_2^-$. This is a weak base equilibrium problem.

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^- \quad K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10}$$

	$C_2H_3O_2^-$		$HC_2H_3O_2$	OH^-
Initial	20.0 mmol/300.0 mL		0	0
	x mol/L $C_2H_3O_2^-$ reacts with H_2O to reach equilibrium			
Change	$-x$	→	$+x$	$+x$
Equil.	$0.0667 - x$		x	x

$$K_b = 5.6\times10^{-10} = \frac{x^2}{0.0667 - x} \approx \frac{x^2}{0.0667},\ x = [OH^-] = 6.1\times10^{-6}\ M$$

pOH = 5.21; pH = 8.79; Assumptions good.

f. mmol OH^- added = 250.0 mL × 0.100 *M* = 25.0 mmol OH^-

	$HC_2H_3O_2$	+	OH^-	→	$C_2H_3O_2^-$ + H_2O
Before	20.0 mmol		25.0 mmol		0
After	0		5.0 mmol		20.0 mmol

After the titration reaction, we have a solution containing excess OH^- and a weak base, $C_2H_3O_2^-$. When a strong base and a weak base are both present, assume the amount of OH^- added from the weak base will be minimal, i.e., the pH past the equivalence point is determined by the amount of excess base.

$$[OH^-]_{excess} = \frac{5.0 \text{ mmol}}{100.0 \text{ mL} + 250.0 \text{ mL}} = 0.014\ M;\ pOH = 1.85;\ pH = 12.15$$

53. a. This is a weak acid/strong base titration. At the halfway point to equivalence, [weak acid] = [conjugate base], so pH = pK_a (always for a weak acid/strong base titration).

$$pH = -\log(6.4 \times 10^{-5}) = 4.19$$

mmol $HC_7H_5O_2$ present = 100. mL × 0.10 M = 10. mmol $HC_7H_5O_2$. For the equivalence point, 10. mmol of OH^- must be added. The volume of OH^- added to reach the equivalence point is:

$$10.\text{ mmol } OH^- \times \frac{1\text{ mL}}{0.10\text{ mmol } OH^-} = 1.0 \times 10^2\text{ mL } OH^-$$

At the equivalence point, 10. mmol of $HC_7H_5O_2$ is neutralized by 10. mmol of OH^- to produce 10. mmol of $C_7H_5O_2^-$. This is a weak base. The total volume of the solution is 100.0 mL + 1.0 × 10^2 mL = 2.0 × 10^2 mL. Solving the weak base equilibrium problem:

$$C_7H_5O_2^- + H_2O \rightleftharpoons HC_7H_5O_2 + OH^- \quad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-5}} = 1.6 \times 10^{-10}$$

	$C_7H_5O_2^-$	$HC_7H_5O_2$	OH^-
Initial	10. mmol/2.0 × 10^2 mL	0	0
Equil.	0.050 - x	x	x

$$K_b = 1.6 \times 10^{-10} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050},\quad x = [OH^-] = 2.8 \times 10^{-6}\ M$$

pOH = 5.55; pH = 8.45 Assumptions good.

b. At the halfway point to equivalence for a weak base/strong acid titration, pH = pK_a since [weak base] = [conjugate acid].

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-4}} = 1.8 \times 10^{-11};\quad pH = pK_a = -\log(1.8 \times 10^{-11}) = 10.74$$

For the equivalence point (mmol acid added = mmol base present):

mmol $C_2H_5NH_2$ present = 100.0 mL × 0.10 M = 10. mmol $C_2H_5NH_2$

$$\text{mL } H^+ \text{ added} = 10.\text{ mmol } H^+ \times \frac{1\text{ mL}}{0.20\text{ mmol } H^+} = 50.\text{ mL } H^+$$

The strong acid added completely converts the weak base into its conjugate acid. Therefore, at the equivalence point, $[C_2H_5NH_3^+]_o$ = 10. mmol/(100.0 + 50.) mL = 0.067 M. Solving the weak acid equilibrium problem:

$$C_2H_5NH_3^+ \rightleftharpoons H^+ + C_2H_5NH_2$$

	$C_2H_5NH_3^+$	H^+	$C_2H_5NH_2$
Initial	0.067 M	0	0
Equil.	0.067 - x	x	x

$$K_a = 1.8 \times 10^{-11} = \frac{x^2}{0.067 - x} \approx \frac{x^2}{0.067},\quad x = [H^+] = 1.1 \times 10^{-6}\ M$$

pH = 5.96; Assumptions good.

c. In a strong acid/strong base titration, the halfway point has no special significance other than exactly one-half of the original amount of acid present has been neutralized.

mmol H^+ present = 100.0 mL × 0.50 M = 50. mmol H^+

$$\text{mL OH}^- \text{ added} = 25.\text{ mmol OH}^- \times \frac{1\text{ mL}}{0.25\text{ mmol}} = 1.0 \times 10^2 \text{ mL OH}^-$$

	H^+	+	OH^-	$\rightarrow$	H_2O
Before	50. mmol		25 mmol		
After	25 mmol		0		

$$[H^+]_{excess} = \frac{25\text{ mmol}}{(100.0 + 1.0 \times 10^2)\text{ mL}} = 0.13\ M;\ \text{pH} = 0.89$$

At the equivalence point of a strong acid/strong base titration, only neutral species are present (Na^+,Cl^-, H_2O) so the pH = 7.00.

54. At equivalence point: 16.00 mL × 0.125 mmol/mL = 2.00 mmol OH^- added; There must be 2.00 mmol HX present initially.

2.00 mL NaOH added = 2.00 mL × 0.125 mmol/mL = 0.250 mmol OH^-; 0.250 mmol of OH^- added will convert 0.250 mmol HX into 0.250 mmol X^-. Remaining HX = 2.00 - 0.250 = 1.75 mmol HX; This is a buffer solution where $[H^+] = 10^{-6.912} = 1.22 \times 10^{-7}\ M$. Since total volume cancels:

$$K_a = \frac{[H^+][X^-]}{[HX]} = \frac{1.22 \times 10^{-7}(0.250)}{1.75} = 1.74 \times 10^{-8}$$

Note: We could also solve for K_a using the Henderson-Hasselbalch equation.

55. a. 1.00 L × 0.100 mol/L = 0.100 mol HCl added to reach stoichiometric point.

The 10.00 g sample must have contained 0.100 mol of NaA. $\frac{10.00\text{ g}}{0.100\text{ mol}} = 100.\text{ g/mol}$

b. 500.0 mL of HCl added represents the halfway point to equivalence. So, pH = pK_a = 5.00 and $K_a = 1.0 \times 10^{-5}$. At the equivalence point, enough H^+ has been added to convert all the A^- present initially into HA. The concentration of HA at the equivalence point is:

$$[HA]_0 = \frac{0.100\text{ mol}}{1.10\text{ L}} = 0.0909\ M$$

	HA	$\rightleftharpoons$	H^+	+	A^-	$K_a = 1.0 \times 10^{-5}$
Initial	0.0909 M		0		0	
Equil.	0.0909 - x		x		x	

$$K_a = 1.0 \times 10^{-5} = \frac{x^2}{0.0909 - x} \approx \frac{x^2}{0.0909}$$

$x = 9.5 \times 10^{-4}\ M = [H^+]$; pH = 3.02 Assumptions good.

Solubility Equilibria

71. In our set-ups, s = solubility in mol/L. Since solids do not appear in the K_{sp} expression, we do not need to worry about their initial or equilibrium amounts.

a.

	$Ag_3PO_4(s)$	$\rightleftharpoons$	$3\ Ag^+(aq)$	+	$PO_4^{3-}(aq)$
Initial			0		0
	s mol/L of $Ag_3PO_4(s)$ dissolves to reach equilibrium				
Change	$-s$	$\rightarrow$	$+3s$		$+s$
Equil.			$3s$		s

$K_{sp} = 1.8 \times 10^{-18} = [Ag^+]^3\,[PO_4^{3-}] = (3s)^3(s) = 27s^4$

$27s^4 = 1.8 \times 10^{-18}$, $s = (6.7 \times 10^{-20})^{1/4} = 1.6 \times 10^{-5}$ mol/L = molar solubility

$$\frac{1.6 \times 10^{-5}\text{ mol } Ag_3PO_4}{\text{L}} \times \frac{418.7\text{ g } Ag_3PO_4}{\text{mol } Ag_3PO_4} = 6.7 \times 10^{-3}\text{ g/L}$$

b.

	$CaCO_3(s)$	$\rightleftharpoons$	$Ca^{2+}(aq)$	+	$CO_3^{2-}(aq)$
Initial	s = solubility (mol/L)		0		0
Equil.			s		s

$K_{sp} = 8.7 \times 10^{-9} = [Ca^{2+}]\,[CO_3^{2-}] = s^2$, $s = 9.3 \times 10^{-5}$ mol/L

$$\frac{9.3 \times 10^{-5}\text{ mol}}{\text{L}} \times \frac{100.1\text{ g}}{\text{mol}} = 9.3 \times 10^{-3}\text{ g/L}$$

c.

	$Hg_2Cl_2(s)$	$\rightleftharpoons$	$Hg_2^{2+}(aq)$	+	$2\ Cl^-(aq)$
Initial	s = solubility (mol/L)		0		0
Equil.			s		$2s$

$K_{sp} = 1.1 \times 10^{-18} = [Hg_2^{2+}]\,[Cl^-]^2 = (s)(2s)^2 = 4s^3$, $s = 6.5 \times 10^{-7}$ mol/L

$$\frac{6.5 \times 10^{-7}\text{ mol}}{\text{L}} \times \frac{472.1\text{ g}}{\text{mol}} = 3.1 \times 10^{-4}\text{ g/L}$$

Challenge Problems

123. mmol $HC_3H_5O_2$ present initially = 45.0 mL × $\frac{0.750\text{ mmol}}{\text{mL}}$ = 33.8 mmol $HC_3H_5O_2$

mmol $C_3H_5O_2^-$ present initially = 55.0 mL × $\frac{0.700\text{ mmol}}{\text{mL}}$ = 38.5 mmol $C_3H_5O_2^-$

The initial pH of the buffer is:

$$pH = pK_a + \log\frac{[C_3H_5O_2^-]}{[HC_3H_5O_2]} = -\log(1.3 \times 10^{-5}) + \log\frac{\frac{38.5\text{ mmol}}{100.0\text{ mL}}}{\frac{33.8\text{ mmol}}{100.0\text{ mL}}} = 4.89 + \log\frac{38.5}{33.8} = 4.95$$

Note: Since the buffer components are in the same volume of solution, we can use the mol (or mmol) ratio in the Henderson-Hasselbalch equation to solve for pH instead of using the concentration ratio of $[C_3H_5O_2^-]/[HC_3H_5O_2]$. The total volume always cancels for buffer solutions.

When NaOH is added, the pH will increase and the added OH^- will convert $HC_3H_5O_2$ into $C_3H_5O_2^-$.

The pH after addition OH^- increases by 2.5%, so the resulting pH is:

$$4.95 + 0.025\,(4.95) = 5.07$$

At this pH, a buffer solution still exists and the mmol ratio between $C_3H_5O_2^-$ and $HC_3H_5O_2$ is:

$$pH = pK_a + \log \frac{\text{mmol } C_3H_5O_2^-}{\text{mmol } HC_3H_5O_2},\quad 5.07 = 4.89 + \log \frac{\text{mmol } C_3H_5O_2^-}{\text{mmol } HC_3H_5O_2}$$

$$\frac{\text{mmol } C_3H_5O_2^-}{\text{mmol } HC_3H_5O_2} = 10^{0.18} = 1.5$$

Let x = mmol OH^- added to increase pH to 5.07. Since OH^- will essentially react to completion with $HC_3H_5O_2$ then the set-up to the problem using mmol is:

	$HC_3H_5O_2$	+	OH^-	$\rightarrow$	$C_3H_5O_2^-$	
Before	33.8 mmol		x mmol		38.5 mmol	
Change	$-x$		$-x$	$\rightarrow$	$+x$	Reacts completely
After	$33.8 - x$		0		$38.5 + x$	

Solving for x:

$$\frac{\text{mmol } C_3H_5O_2^-}{\text{mmol } HC_3H_5O_2} = 1.5 = \frac{38.5 + x}{33.8 - x},\quad 1.5\,(33.8 - x) = 38.5 + x,\quad x = 4.9 \text{ mmol } OH^- \text{ added}$$

The volume of NaOH necessary to raise the pH by 2.5% is:

$$4.9 \text{ mmol NaOH} \times \frac{1 \text{ mL}}{0.10 \text{ mmol NaOH}} = 49 \text{ mL}$$

49 mL of 0.10 M NaOH must be added to increase the pH by 2.5%.

131. For HOCl, $K_a = 3.5 \times 10^{-8}$ and $pK_a = -\log(3.5 \times 10^{-8}) = 7.46$. This will be a buffer solution since the pH is close to the pK_a value.

$$pH = pK_a + \log \frac{[OCl^-]}{[HOCl]},\quad 8.00 = 7.46 + \log \frac{[OCl^-]}{[HOCl]},\quad \frac{[OCl^-]}{[HOCl]} = 10^{0.54} = 3.5$$

1.00 L × 0.0500 M = 0.0500 mol HOCl initially. Added OH^- converts HOCl into OCl^-. The total moles of OCl^- and HOCl must equal 0.0500 mol. Solving where n = moles:

$$n_{OCl^-} + n_{HOCl} = 0.0500 \text{ and } n_{OCl^-} = 3.5\, n_{HOCl}$$

$$4.5\, n_{HOCl} = 0.0500,\quad n_{HOCl} = 0.011 \text{ mol};\quad n_{OCl^-} = 0.039 \text{ mol}$$

Need to add 0.039 mol NaOH to produce 0.039 mol OCl^-.

$$0.039 \text{ mol} = V \times 0.0100\, M,\ V = 3.9 \text{ L NaOH}$$

Note: Normal buffer assumptions hold.

Chapter 10: #43, 115, 116

Entropy and the Second Law of Thermodynamics: Free Energy

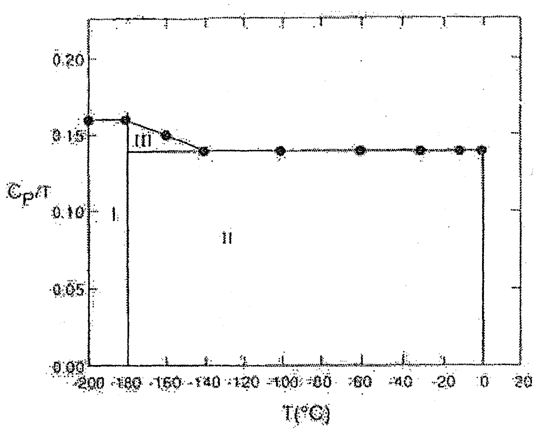
43. $-144\ J/K = (2\ mol)S^\circ_{AlBr_3} - [2(28\ J/K) + 3(152\ J/K)]$, $S^\circ_{AlBr_3} = 184\ J\ K^{-1}\ mol^{-1}$

Challenge Problems

115.

T(°C)	T(K)	$C_p(J\ K^{-1}\ mol^{-1})$	$C_p/T\ (J\ K^{-2}\ mol^{-1})$
-200.	73	12	0.16
-180.	93	15	0.16
-160.	113	17	0.15
-140.	133	19	0.14
-100.	173	24	0.14
-60.	213	29	0.14
-30.	243	33	0.14
-10.	263	36	0.14
0	273	37	0.14

Total area of C_p/T vs T plot = ΔS = I + II + III (See following plot.)



$\Delta S = (0.16\ J\ K^{-2}\ mol^{-1})(20.\ K) + (0.14\ J\ K^{-2}\ mol^{-1})(180.\ K) + 1/2(0.02\ J\ K^{-2}\ mol^{-1})(40.\ K)$

$\Delta S = 3.2 + 25 + 0.4 = 29\ J\ K^{-1}\ mol^{-1}$

116. We can set up 3 equations in 3 unknowns:

$$28.7262 = a + 300.0\,b + (300.0)^2\,c$$

$$29.2937 = a + 400.0\,b + (400.0)^2\,c$$

$$29.8545 = a + 500.0\,b + (500.0)^2\,c$$

These can be solved by several methods. One way involves setting up a matrix and solving with a calculator such as:

$$\begin{pmatrix} 1 & 300.0 & 90{,}000 \\ 1 & 400.0 & 160{,}000 \\ 1 & 500.0 & 250{,}000 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} 28.7262 \\ 29.2937 \\ 29.8545 \end{pmatrix}$$

The solution is: $a = 26.98$; $b = 5.91 \times 10^{-3}$; $c = -3.4 \times 10^{-7}$

At 900. K: $C_p = 26.98 + 5.91 \times 10^{-3}(900.) - 3.4 \times 10^{-7}(900.)^2 = 32.02\ \text{J K}^{-1}\,\text{mol}^{-1}$

$$\Delta S = n\int_{T_1}^{T_2} \frac{C_P dT}{T} = n\int_{T_1}^{T_2} \frac{(a + bT + cT^2)}{T}\,dT, \quad n = 1.00\ \text{mol}$$

$$\Delta S = a\int_{T_1}^{T_2} \frac{dT}{T} + b\int_{T_1}^{T_2} dT + c\int_{T_1}^{T_2} T\,dT = a \ln\left(\frac{T_2}{T_1}\right) + b\,(T_2 - T_1) + \frac{c(T_2^2 - T_1^2)}{2}$$

Solving using $T_2 = 900.$ K and $T_1 = 100.$ K: $\Delta S = 59.3 + 4.73 - 0.14 = 63.9$ J/K