

photometer, and its absorbance was found to be 0.780. Using these data, we want to calculate the percent manganese in the steel. The  $\text{MnO}_4^-$  ions from the manganese in the dissolved steel sample show an absorbance of 0.780. Using the Beer-Lambert law, we calculate the concentration of  $\text{MnO}_4^-$  in this solution:

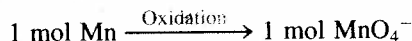
$$c = \frac{A}{\epsilon l} = \frac{0.780}{2.48 \times 10^3 \text{ L/mol}} \times 3.15 \times 10^{-4} \text{ mol/L}$$

There is a more direct way for finding  $c$ . Using a graph such as that in Fig. A.7 (often called a *Beer's law plot*), we can read the concentration that corresponds to  $A = 0.780$ . This interpolation is shown by dashed lines on the graph. By this method,  $c = 3.15 \times 10^{-4} \text{ mol/L}$ , which agrees with the value obtained above.

Recall that the original 0.1523-g steel sample was dissolved, the manganese was converted to permanganate, and the volume was adjusted to 100.0 mL. We now know that  $[\text{MnO}_4^-]$  in that solution is  $3.15 \times 10^{-4} \text{ M}$ . Using this concentration, we can calculate the total number of moles of  $\text{MnO}_4^-$  in that solution:

$$\begin{aligned} \text{mol MnO}_4^- &= 100.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 3.15 \times 10^{-4} \frac{\text{mol}}{\text{L}} \\ &= 3.15 \times 10^{-5} \text{ mol} \end{aligned}$$

Since each mole of manganese in the original steel sample yields a mole of  $\text{MnO}_4^-$ , that is,



the original steel sample must have contained  $3.15 \times 10^{-5}$  mole of manganese. The mass of manganese present in the sample is

$$3.15 \times 10^{-5} \text{ mol Mn} \times \frac{54.938 \text{ g of Mn}}{1 \text{ mol Mn}} = 1.73 \times 10^{-3} \text{ g of Mn}$$

Since the steel sample weighed 0.1523 g, the present manganese in the steel is

$$\frac{1.73 \times 10^{-3} \text{ g of Mn}}{1.523 \times 10^{-1} \text{ g of sample}} \times 100 = 1.14\%$$

This example illustrates a typical use of spectroscopy in quantitative analysis. The steps commonly involved are as follows:

1. Preparation of a calibration plot (a Beer's law plot) by measuring the absorbance values of a series of solutions with known concentrations
2. Measurement of the absorbance of the solution of unknown concentration
3. Use of the calibration plot to determine the unknown concentration

## APPENDIX 4

## Selected Thermodynamic Data

Note: All values are assumed precise to at least  $\pm 1$ .

Substance and State	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/K · mol)
Aluminum			
Al(s)	0	0	28
Al <sub>2</sub> O <sub>3</sub> (s)	-1676	-1582	51
Al(OH) <sub>3</sub> (s)	-1277		
AlCl <sub>3</sub> (s)	-704	-629	111

Substance and State	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/K · mol)
Barium			
Ba(s)	0	0	67
BaCO <sub>3</sub> (s)	-1219	-1139	112
BaO(s)	-582	-552	70
Ba(OH) <sub>2</sub> (s)	-946		

(continued)

## Appendix Four (continued)

Substance and State	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/K · mol)
<i>Barium, continued</i>			
BaSO <sub>4</sub> (s)	-1465	-1353	132
<i>Beryllium</i>			
Be(s)	0	0	10
BeO(s)	-599	-569	14
Be(OH) <sub>2</sub> (s)	-904	-815	47
<i>Bromine</i>			
Br <sub>2</sub> (l)	0	0	152
Br <sub>2</sub> (g)	31	3	245
Br <sub>2</sub> (aq)	-3	4	130
Br <sup>-</sup> (aq)	-121	-104	82
HBr(g)	-36	-53	199
<i>Cadmium</i>			
Cd(s)	0	0	52
CdO(s)	-258	-228	55
Cd(OH) <sub>2</sub> (s)	-561	-474	96
CdS(s)	-162	-156	65
CdSO <sub>4</sub> (s)	-935	-823	123
<i>Calcium</i>			
Ca(s)	0	0	41
CaC <sub>2</sub> (s)	-63	-68	70
CaCO <sub>3</sub> (s)	-1207	-1129	93
CaO(s)	-635	-604	40
Ca(OH) <sub>2</sub> (s)	-987	-899	83
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (s)	-4126	-3890	241
CaSO <sub>4</sub> (s)	-1433	-1320	107
CaSiO <sub>3</sub> (s)	-1630	-1550	84
<i>Carbon</i>			
C(s) (graphite)	0	0	6
C(s) (diamond)	2	3	2
CO(g)	-110.5	-137	198
CO <sub>2</sub> (g)	-393.5	-394	214
CH <sub>4</sub> (g)	-75	-51	186
CH <sub>3</sub> OH(g)	-201	-163	240
CH <sub>3</sub> OH(l)	-239	-166	127
H <sub>2</sub> CO(g)	-116	-110	219
HCOOH(g)	-363	-351	249
HCN(g)	135.1	125	202
C <sub>2</sub> H <sub>2</sub> (g)	227	209	201
C <sub>2</sub> H <sub>4</sub> (g)	52	68	219
CH <sub>3</sub> CHO(g)	-166	-129	250
C <sub>2</sub> H <sub>5</sub> OH(l)	-278	-175	161
C <sub>2</sub> H <sub>6</sub> (g)	-84.7	-32.9	229.5
C <sub>3</sub> H <sub>6</sub> (g)	20.9	62.7	266.9
C <sub>3</sub> H <sub>8</sub> (g)	-104	-24	270
C <sub>2</sub> H <sub>4</sub> O(g) (ethylene oxide)	-53	-13	242
CH <sub>2</sub> =CHCN(g)	185.0	195.4	274
CH <sub>3</sub> COOH(l)	-484	-389	160
C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> (s)	-1275	-911	212
CCl <sub>4</sub>	-135	-65	216
<i>Chlorine</i>			
Cl <sub>2</sub> (g)	0	0	223
Cl <sub>2</sub> (aq)	-23	7	121

Substance and State	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/K · mol)
<i>Chlorine, continued</i>			
Cl <sup>-</sup> (aq)	-167	-131	57
HCl(g)	-92	-95	187
<i>Chromium</i>			
Cr(s)	0	0	24
Cr <sub>2</sub> O <sub>3</sub> (s)	-1128	-1047	81
CrO <sub>3</sub> (s)	-579	-502	72
<i>Copper</i>			
Cu(s)	0	0	33
CuCO <sub>3</sub> (s)	-595	-518	88
Cu <sub>2</sub> O(s)	-170	-148	93
CuO(s)	-156	-128	43
Cu(OH) <sub>2</sub> (s)	-450	-372	108
CuS(s)	-49	-49	67
<i>Fluorine</i>			
F <sub>2</sub> (g)	0	0	203
F <sub>2</sub> (aq)	-333	-279	-14
HF(g)	-271	-273	174
<i>Hydrogen</i>			
H <sub>2</sub> (g)	0	0	131
H(g)	217	203	115
H <sup>+</sup> (aq)	0	0	0
OH <sup>-</sup> (aq)	-230	-157	-11
H <sub>2</sub> O(l)	-286	-237	70
H <sub>2</sub> O(g)	-242	-229	189
<i>Iodine</i>			
I <sub>2</sub> (s)	0	0	116
I <sub>2</sub> (g)	62	19	261
I <sub>2</sub> (aq)	23	16	137
I <sup>-</sup> (aq)	-55	-52	106
<i>Iron</i>			
Fe(s)	0	0	27
Fe <sub>3</sub> C(s)	21	15	108
Fe <sub>0.95</sub> O(s) (wustite)	-264	-240	59
FeO	-272	-255	61
Fe <sub>3</sub> O <sub>4</sub> (s) (magnetite)	-1117	-1013	146
Fe <sub>2</sub> O <sub>3</sub> (s) (hematite)	-826	-740	90
FeS(s)	-95	-97	67
FeS <sub>2</sub> (s)	-178	-166	53
FeSO <sub>4</sub> (s)	-929	-825	121
<i>Lead</i>			
Pb(s)	0	0	65
PbO <sub>2</sub> (s)	-277	-217	69
PbS(s)	-100	-99	91
PbSO <sub>4</sub> (s)	-920	-813	149
<i>Magnesium</i>			
Mg(s)	0	0	33
MgCO <sub>3</sub> (s)	-1113	-1029	66
MgO(s)	-602	-569	27
Mg(OH) <sub>2</sub> (s)	-925	-834	64
<i>Manganese</i>			
Mn(s)	0	0	32

Substance and State	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/K · mol)
<i>Manganese, continued</i>			
MnO(s)	-385	-363	60
Mn <sub>3</sub> O <sub>4</sub> (s)	-1387	-1280	149
Mn <sub>2</sub> O <sub>3</sub> (s)	-971	-893	110
MnO <sub>2</sub> (s)	-521	-466	53
MnO <sub>4</sub> <sup>-</sup> (aq)	-543	-449	190
<i>Mercury</i>			
Hg(l)	0	0	76
Hg <sub>2</sub> Cl <sub>2</sub> (s)	-265	-211	196
HgCl <sub>2</sub> (s)	-230	-184	144
HgO(s)	-90	-59	70
HgS(s)	-58	-49	78
<i>Nickel</i>			
Ni(s)	0	0	30
NiCl <sub>2</sub> (s)	-316	-272	107
NiO(s)	-241	-213	38
Ni(OH) <sub>2</sub> (s)	-538	-453	79
NiS(s)	-93	-90	53
<i>Nitrogen</i>			
N <sub>2</sub> (g)	0	0	192
NH <sub>3</sub> (g)	-46	-17	193
NH <sub>3</sub> (aq)	-80	-27	111
NH <sub>4</sub> <sup>+</sup> (aq)	-132	-79	113
NO(g)	90	87	211
NO <sub>2</sub> (g)	34	52	240
N <sub>2</sub> O(g)	82	104	220
N <sub>2</sub> O <sub>4</sub> (g)	10	98	304
N <sub>2</sub> O <sub>4</sub> (l)	-20	97	209
N <sub>2</sub> O <sub>5</sub> (s)	-42	134	178
N <sub>2</sub> H <sub>4</sub> (l)	51	149	121
N <sub>2</sub> H <sub>3</sub> CH <sub>3</sub> (l)	54	180	166
HNO <sub>3</sub> (aq)	-207	-111	146
HNO <sub>3</sub> (l)	-174	-81	156
NH <sub>4</sub> ClO <sub>4</sub> (s)	-295	-89	186
NH <sub>4</sub> Cl(s)	-314	-203	96
<i>Oxygen</i>			
O <sub>2</sub> (g)	0	0	205
O(g)	249	232	161
O <sub>3</sub> (g)	143	163	239
<i>Phosphorus</i>			
P(s) (white)	0	0	41
P(s) (red)	-18	-12	23
P(s) (black)	-39	-33	23
P <sub>4</sub> (g)	59	24	280
PF <sub>5</sub> (g)	-1578	-1509	296
PH <sub>3</sub> (g)	5	13	210
H <sub>3</sub> PO <sub>4</sub> (s)	-1279	-1119	110
H <sub>3</sub> PO <sub>4</sub> (l)	-1267	—	—
H <sub>3</sub> PO <sub>4</sub> (aq)	-1288	-1143	158
P <sub>4</sub> O <sub>10</sub> (s)	-2984	-2698	229
<i>Potassium</i>			
K(s)	0	0	64
KCl(s)	-436	-408	83

Substance and State	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/K · mol)
<i>Potassium, continued</i>			
KClO <sub>3</sub> (s)	-391	-290	143
KClO <sub>4</sub> (s)	-433	-304	151
K <sub>2</sub> O(s)	-361	-322	98
K <sub>2</sub> O <sub>2</sub> (s)	-496	-430	113
KO <sub>2</sub> (s)	-283	-238	117
KOH(s)	-425	-379	79
KOH(aq)	-481	-440	9.20
<i>Silicon</i>			
SiO <sub>2</sub> (s) (quartz)	-911	-856	42
SiCl <sub>4</sub> (l)	-687	-620	240
<i>Silver</i>			
Ag(s)	0	0	43
Ag <sup>+</sup> (aq)	105	77	73
AgBr(s)	-100	-97	107
AgCN(s)	146	164	84
AgCl(s)	-127	-110	96
Ag <sub>2</sub> CrO <sub>4</sub> (s)	-712	-622	217
AgI(s)	-62	-66	115
Ag <sub>2</sub> O(s)	-31	-11	122
Ag <sub>2</sub> S(s)	-32	-40	146
<i>Sodium</i>			
Na(s)	0	0	51
Na <sup>+</sup> (aq)	-240	-262	59
NaBr(s)	-360	-347	84
Na <sub>2</sub> CO <sub>3</sub> (s)	-1131	-1048	136
NaHCO <sub>3</sub> (s)	-948	-852	102
NaCl(s)	-411	-384	72
NaH(s)	-56	-33	40
NaI(s)	-288	-282	91
NaNO <sub>2</sub> (s)	-359	—	—
NaNO <sub>3</sub> (s)	-467	-366	116
Na <sub>2</sub> O(s)	-416	-377	73
Na <sub>2</sub> O <sub>2</sub> (s)	-515	-451	95
NaOH(s)	-427	-381	64
NaOH(aq)	-470	-419	50
<i>Sulfur</i>			
S(s) (rhombic)	0	0	32
S(s) (monoclinic)	0.3	0.1	33
S <sup>2-</sup> (aq)	33	86	215
S <sub>8</sub> (g)	102	50	431
SF <sub>6</sub> (g)	-1209	-1105	292
H <sub>2</sub> S(g)	-21	-34	206
SO <sub>2</sub> (g)	-297	-300	248
SO <sub>3</sub> (g)	-396	-371	257
SO <sub>4</sub> <sup>2-</sup> (aq)	-909	-745	20
H <sub>2</sub> SO <sub>4</sub> (l)	-814	-690	157
H <sub>2</sub> SO <sub>4</sub> (aq)	-909	-745	20
<i>Tin</i>			
Sn(s) (white)	0	0	52
Sn(s) (gray)	22	0.1	44
SnO(s)	-285	-257	56
SnO <sub>2</sub> (s)	-581	-520	52

(continued)

## Appendix Four (continued)

Substance and State	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/K · mol)
Tin, <i>continued</i>			
Sn(OH) <sub>2</sub> (s)	-561	-492	155
Titanium			
TiCl <sub>4</sub> (g)	-763	-727	355
TiO <sub>2</sub> (s)	-945	-890	50
Uranium			
U(s)	0	0	50
UF <sub>6</sub> (s)	-2137	-2008	228
UF <sub>6</sub> (g)	-2113	-2029	380
UO <sub>2</sub> (s)	-1084	-1029	78
U <sub>3</sub> O <sub>8</sub> (s)	-3575	-3393	282
UO <sub>3</sub> (s)	-1230	-1150	99

Substance and State	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/K · mol)
Xenon			
Xe(g)	0	0	170
XeF <sub>2</sub> (g)	-108	-48	254
XeF <sub>4</sub> (s)	-251	-121	146
XeF <sub>6</sub> (g)	-294		
XeO <sub>3</sub> (s)	402		
Zinc			
Zn(s)	0	0	42
ZnO(s)	-348	-318	44
Zn(OH) <sub>2</sub> (s)	-642		
ZnS(s) (wurtzite)	-193		
ZnS(s) (zinc blende)	-206	-201	58
ZnSO <sub>4</sub> (s)	-983	-874	120

## APPENDIX 5

## Equilibrium Constants and Reduction Potentials

A5.1 Values of  $K_a$  for Some Common Monoprotic Acids

Name	Formula	Value of $K_a$
Hydrogen sulfate ion	HSO <sub>4</sub> <sup>-</sup>	$1.2 \times 10^{-2}$
Chlorous acid	HClO <sub>2</sub>	$1.2 \times 10^{-2}$
Monochloroacetic acid	HC <sub>2</sub> H <sub>2</sub> ClO <sub>2</sub>	$1.35 \times 10^{-3}$
Hydrofluoric acid	HF	$7.2 \times 10^{-4}$
Nitrous acid	HNO <sub>2</sub>	$4.0 \times 10^{-4}$
Formic acid	HCO <sub>2</sub> H	$1.8 \times 10^{-4}$
Lactic acid	HC <sub>3</sub> H <sub>5</sub> O <sub>3</sub>	$1.38 \times 10^{-4}$
Benzoic acid	HC <sub>7</sub> H <sub>5</sub> O <sub>2</sub>	$6.4 \times 10^{-5}$
Acetic acid	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	$1.8 \times 10^{-5}$
Hydrated aluminum(III) ion	[Al(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	$1.4 \times 10^{-5}$
Propanoic acid	HC <sub>3</sub> H <sub>5</sub> O <sub>2</sub>	$1.3 \times 10^{-5}$
Hypochlorous acid	HOCl	$3.5 \times 10^{-8}$
Hypobromous acid	HOBr	$2 \times 10^{-9}$
Hydrocyanic acid	HCN	$6.2 \times 10^{-10}$
Boric acid	H <sub>3</sub> BO <sub>3</sub>	$5.8 \times 10^{-10}$
Ammonium ion	NH <sub>4</sub> <sup>+</sup>	$5.6 \times 10^{-10}$
Phenol	HOC <sub>6</sub> H <sub>5</sub>	$1.6 \times 10^{-10}$
Hypoiodous acid	HOI	$2 \times 10^{-11}$