(b) We can find the absorbance at a given temperature from the equation of the line in (a): $\ln A = -4\,813\,(1/T) + 14.90$. At 31.8°C, $1/T = 0.003\,279\ \text{K}^{-1}$, giving $\ln A = -0.882\,9$, or $A = 0.413_6$. To find the molar absorptivity, we need to convert the pressure of toluene into a concentration in mol/L. The vapor pressure is $\frac{40.0\ \text{Torr}}{760\ \text{Torr/atm}} \frac{1.013\,25\ \text{bar}}{\text{atm}} = 0.053\,3_3$ bar. From the ideal gas law, we can say

$$\frac{\text{mol}}{\text{L}} = \frac{n}{V} = \frac{P}{RT} = \frac{0.053\,3_3\ \text{bar}}{(0.083\,145\ \text{L·bar/mol·K})(304.9_5\ \text{K})} = 2.10_3 \times 10^{-3}\ \text{M}.$$

The molar absorptivity is $\varepsilon = \frac{A}{bc} = \frac{0.413_6}{(1.00\ \text{cm})(2.10_3 \times 10^{-3}\ \text{M})} = 1.97 \times 10^2\ \text{M}^{-1}\text{cm}^{-1}$.

18-15. Neocuproine reacts with Cu(I) and prevents it from forming a complex with ferrozine that would give a false positive result in the analysis of iron.

18-16. (a) $c = A/\varepsilon b = 0.427/[(6\,130\ \text{M}^{-1}\ \text{cm}^{-1})(1.000\ \text{cm})] = 6.97 \times 10^{-5}\ \text{M}$

(b) The sample had been diluted × 10 $\Rightarrow$ 6.97×10^{-4} M

(c) $$\frac{x\ \text{g}}{(292.16\ \text{g/mol})(5.00 \times 10^{-3}\ \text{L})} = 6.97 \times 10^{-4}\ \text{M} \Rightarrow x = 1.02\ \text{mg}$$

18-17. Yes.

18-18. (a) $$\varepsilon = \frac{A}{cb} = \frac{0.267 - 0.019}{(3.15 \times 10^{-6}\ \text{M})(1.000\ \text{cm})} = 7.87 \times 10^4\ \text{M}^{-1}\ \text{cm}^{-1}$$

(b) $$c = \frac{A}{\varepsilon b} = \frac{0.175 - 0.019}{(7.87 \times 10^4\ \text{M}^{-1}\ \text{cm}^{-1})(1.000\ \text{cm})} = 1.98 \times 10^{-6}\ \text{M}$$

18-19. (a) The absorbance due to the colored product from nitrite added to sample C is $0.967 - 0.622 = 0.345$. The concentration of colored product due to added nitrite in sample C is $\frac{(7.50 \times 10^{-3}\ \text{M})(10.0 \times 10^{-6}\ \text{L})}{0.054\ \text{L}} = 1.389 \times 10^{-6}$ M

$$\varepsilon = A/bc = 0.345/[(1.389 \times 10^{-6})(5.00)] = 4.97 \times 10^4\ \text{M}^{-1}\ \text{cm}^{-1}$$

(b) 7.50×10^{-8} mol of nitrite (from 10.0 μL added to sample C) gives $A = 0.345$. In sample B, x mole of nitrite in food extract gives $A = 0.622 - 0.153 = 0.469$.

$$\frac{x\ \text{mol}}{7.50 \times 10^{-8}\ \text{mol}} = \frac{0.469}{0.345} \Rightarrow x = 1.020 \times 10^{-7}\ \text{mol}\ NO_2^- = 4.69\ \mu\text{g}$$

18-20.

Curve	Absorbance Measured on Graph	$[Fe^{3+}]$ (ng/mL)
a	0.084	0
b	0.278	0.40
c	0.472	0.80
d	0.666	1.20
e	0.860	1.60

(a) A graph of absorbance vs $[Fe^{3+}]$(ng/mL) has a slope (k) of 0.485 and an intercept (b) of 0.084.

(b) $[Fe^{3+}]$ in final solution $= \frac{1}{k}(A_t - b) = \left(\frac{1}{0.485}\right)(0.515 - 0.084) = 0.889$ ng/mL. But the unknown was diluted from 5.00 to 26.00 mL.

Therefore $[Fe^{3+}]$ in unknown $= \left(\frac{26.00}{5.00}\right)(0.889) = 4.6_2$ ng/mL $= 82._7$ nM.

18-21. $n \rightarrow \pi^*(T_1)$:

$$E = h\nu = h\frac{c}{\lambda} = (6.626\,1 \times 10^{-34}\ \text{J·s})\frac{2.997\,9 \times 10^8\ \text{s}^{-1}}{397 \times 10^{-9}\ \text{m}} = 5.00 \times 10^{-19}\ \text{J}$$

To convert to J/mol, multiply by Avogadro's number:

5.00×10^{-19} J/molecule $\times 6.022 \times 10^{23}$ molecules/mol = 301 kJ/mol.

$n \rightarrow \pi^*(S_1)$:

$$E = (6.626\,1 \times 10^{-34}\ \text{J·s})\frac{2.997\,9 \times 10^8\ \text{s}^{-1}}{355 \times 10^{-9}\ \text{m}} = 5.60 \times 10^{-19}\ \text{J} = 337\ \text{kJ/mol}.$$

The difference between the T_1 and S_1 states is 337 – 301 = 36 kJ/mol.

18-22. Fluorescence is emission of light with no change in the electronic spin state of the molecule (e. g. singlet → singlet). In phosphorescence, the electronic spin does change during emission (e. g. triplet → singlet). Phosphorescence is less probable, so molecules spend more time in the excited state prior to phosphorescence than to fluorescence. That is, phosphorescence has a longer lifetime than fluorescence. Phosphorescence also comes at lower energy (longer wavelength) than fluorescence, because the triplet excited state is at lower energy than the singlet excited state.

18-23. Luminescence is light given off after a molecule absorbs light. Chemiluminscence is light given off by a molecule created in an excited state in a chemical reaction.

18-24. Phosphorescence is emitted at longer wavelength than fluorescence. Absorption is at shortest wavelength.