

## Problems\*

## Numerical problems

**6.1** The equilibrium constant for the reaction,  $\text{I}_2(\text{s}) + \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{IBr}(\text{g})$  is 0.164 at 25°C. (a) Calculate  $\Delta_r G^\circ$  for this reaction. (b) Bromine gas is introduced into a container with excess solid iodine. The pressure and temperature are held at 0.164 atm and 25°C, respectively. Find the partial pressure of  $\text{IBr}(\text{g})$  at equilibrium. Assume that all the bromine is in the liquid form and that the vapour pressure of iodine is negligible. (c) In fact, solid iodine has a measurable vapour pressure at 25°C. In this case, how would the calculation have to be modified?

**6.2** Consider the dissociation of methane,  $\text{CH}_4(\text{g})$ , into the elements  $\text{H}_2(\text{g})$  and  $\text{C}(\text{s, graphite})$ . (a) Given that  $\Delta_f H^\circ(\text{CH}_4, \text{g}) = -74.85 \text{ kJ mol}^{-1}$  and that  $\Delta_f S^\circ(\text{CH}_4, \text{g}) = -80.67 \text{ J K}^{-1} \text{ mol}^{-1}$  at 298 K, calculate the value of the equilibrium constant at 298 K. (b) Assuming that  $\Delta_f H^\circ$  is independent of temperature, calculate  $K$  at 50°C. (c) Calculate the degree of dissociation,  $\alpha$ , of methane at 25°C and a total pressure of 0.010 bar. (d) Without doing any numerical calculations, explain how the degree of dissociation for this reaction will change as the pressure and temperature are varied.

**6.3** The equilibrium pressure of  $\text{H}_2$  over  $\text{U}(\text{s})$  and  $\text{UH}_3(\text{s})$  between 450 K and 715 K fits the expression  $\ln(p/\text{Pa}) = A + B/T + C \ln(T/\text{K})$ , with  $A = 69.32$ ,  $B = -1.464 \times 10^4 \text{ K}$ , and  $C = -5.65$ . Find an expression for the standard enthalpy of formation of  $\text{UH}_3(\text{s})$  and from it calculate  $\Delta_f C_p^\circ$ .

**6.4** The degree of dissociation,  $\alpha$ , of  $\text{CO}_2(\text{g})$  into  $\text{CO}(\text{g})$  and  $\text{O}_2(\text{g})$  at high temperatures was found to vary with temperature as follows:

$T/\text{K}$	1395	1443	1498
$\alpha/10^{-4}$	1.44	2.50	4.71

Assuming  $\Delta_f H^\circ$  to be constant over this temperature range, calculate  $K$ ,  $\Delta_f G^\circ$ ,  $\Delta_f H^\circ$ , and  $\Delta_f S^\circ$ . Make any justifiable approximations.

**6.5** The standard reaction enthalpy for the decomposition of  $\text{CaCl}_2 \cdot \text{NH}_3(\text{s})$  into  $\text{CaCl}_2(\text{s})$  and  $\text{NH}_3(\text{g})$  is nearly constant at  $+78 \text{ kJ mol}^{-1}$  between 350 K and 470 K. The equilibrium pressure of  $\text{NH}_3$  in the presence of  $\text{CaCl}_2 \cdot \text{NH}_3$  is 1.71 kPa at 400 K. Find an expression for the temperature dependence of  $\Delta_r G^\circ$  in the same range.

**6.6** Calculate the equilibrium constant of the reaction  $\text{CO}(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{H}_2\text{CO}(\text{g})$  given that, for the production of liquid formaldehyde,  $\Delta_f G^\circ = +28.95 \text{ kJ mol}^{-1}$  at 298 K and that the vapour pressure of formaldehyde is 1500 Torr at that temperature.

**6.7** Acetic acid was evaporated in a container of volume  $21.45 \text{ cm}^3$  at 437 K and at an external pressure of 101.9 kPa, and the container was then sealed. The combined mass of acid monomer and dimer in the sealed container was 0.0463 g. The experiment was repeated with the same container but at 471 K, and the combined mass of acid monomer and dimer was found to be 0.0380 g. Calculate the equilibrium constant for the dimerization of the acid in the vapour and the enthalpy of dimerization.

**6.8** A sealed container was filled with 0.300 mol  $\text{H}_2(\text{g})$ , 0.400 mol  $\text{I}_2(\text{g})$ , and 0.200 mol  $\text{HI}(\text{g})$  at 870 K and total pressure 1.00 bar. Calculate the amounts of the components in the mixture at equilibrium given that  $K = 870$  for the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$ .

**6.9** The dissociation of  $\text{I}_2$  can be monitored by measuring the total pressure, and three sets of results are as follows:

$T/\text{K}$	973	1073	1173
100p/atm	6.244	7.500	9.181
$10^4 n_1$	2.4709	2.4555	2.4366

where  $n_1$  is the amount of I atoms per mole of  $\text{I}_2$  molecules in the mixture, which occupied  $342.68 \text{ cm}^3$ . Calculate the equilibrium constants of the dissociation and the standard enthalpy of dissociation at the mean temperature.

**6.10†** Thorn *et al.* (*J. Phys. Chem.* **100**, 14178 (1996)) carried out a study of  $\text{Cl}_2\text{O}(\text{g})$  by photoelectron ionization. From their measurements, they report  $\Delta_f H^\circ(\text{Cl}_2\text{O}) = +77.2 \text{ kJ mol}^{-1}$ . They combined this measurement with literature data on the reaction  $\text{Cl}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow 2 \text{HOCl}(\text{g})$ , for which  $K = 8.2 \times 10^{-2}$  and  $\Delta_r S^\circ = +16.38 \text{ J K}^{-1} \text{ mol}^{-1}$ , and with readily available thermodynamic data on water vapour to report a value for  $\Delta_f H^\circ(\text{HOCl})$ . Calculate that value. All quantities refer to 298 K.

**6.11†** The 1980s saw reports of  $\Delta_f H^\circ(\text{SiH}_2)$  ranging from 243 to 289  $\text{kJ mol}^{-1}$ . If the standard enthalpy of formation is uncertain by this amount, by what factor is the equilibrium constant for the formation of  $\text{SiH}_2$  from its elements uncertain at (a) 298 K, (b) 700 K?

**6.12** Fuel cells provide electrical power for spacecraft (as in the NASA space shuttles) and also show promise as power sources for automobiles. Hydrogen and carbon monoxide have been investigated for use in fuel cells, so their solubilities in molten salts are of interest. Their solubilities in a molten  $\text{NaNO}_3/\text{KNO}_3$  mixture were found to fit the following expressions:

$$\log s_{\text{H}_2} = -5.39 - \frac{768}{T/\text{K}} \quad \log s_{\text{CO}} = -5.98 - \frac{980}{T/\text{K}}$$

where  $s$  is the solubility in  $\text{mol cm}^{-3} \text{ bar}^{-1}$ . Calculate the standard molar enthalpies of solution of the two gases at 570 K.

**6.13** Given that  $\Delta_f G^\circ = -212.7 \text{ kJ mol}^{-1}$  for the reaction in the Daniell cell at 25°C, and  $b(\text{CuSO}_4) = 1.0 \times 10^{-3} \text{ mol kg}^{-1}$  and  $b(\text{ZnSO}_4) = 3.0 \times 10^{-3} \text{ mol kg}^{-1}$ , calculate (a) the ionic strengths of the solutions, (b) the mean ionic activity coefficients in the compartments, (c) the reaction quotient, (d) the standard cell potential, and (e) the cell potential. (Take  $\gamma_+ = \gamma_- = \gamma_{\pm}$  in the respective compartments.)

**6.14** A fuel cell develops an electric potential from the chemical reaction between reagents supplied from an outside source. What is the cell potential of a cell fuelled by (a) hydrogen and oxygen, (b) the combustion of butane at 1.0 bar and 298 K?

**6.15** Although the hydrogen electrode may be conceptually the simplest electrode and is the basis for our reference state of electrical potential in electrochemical systems, it is cumbersome to use. Therefore, several substitutes for it have been devised. One of these alternatives is the quinhydrone electrode (quinhydrone,  $\text{Q} \cdot \text{QH}_2$ , is a complex of quinone,  $\text{C}_6\text{H}_4\text{O}_2 = \text{Q}$ , and hydroquinone,  $\text{C}_6\text{H}_4\text{O}_2\text{H}_2 = \text{QH}_2$ ). The electrode half-reaction is  $\text{Q}(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{QH}_2(\text{aq})$ ,  $E^\circ = +0.6994 \text{ V}$ . If the cell  $\text{Hg}|\text{Hg}_2\text{Cl}_2(\text{s})|\text{HCl}(\text{aq})|\text{Q} \cdot \text{QH}_2|\text{Au}$  is prepared, and the measured cell potential is  $+0.190 \text{ V}$ , what is the pH of the HCl solution? Assume that the Debye–Hückel limiting law is applicable.

**6.16** Consider the cell,  $\text{Zn}(\text{s})|\text{ZnCl}_2(0.0050 \text{ mol kg}^{-1})|\text{Hg}_2\text{Cl}_2(\text{s})|\text{Hg}(\text{l})$ , for which the cell reaction is  $\text{Hg}_2\text{Cl}_2(\text{s}) + \text{Zn}(\text{s}) \rightarrow 2 \text{Hg}(\text{l}) + 2 \text{Cl}^-(\text{aq}) + \text{Zn}^{2+}(\text{aq})$ . Given that  $E^\circ(\text{Zn}^{2+}, \text{Zn}) = -0.7628 \text{ V}$ ,  $E^\circ(\text{Hg}_2\text{Cl}_2, \text{Hg}) = +0.2676 \text{ V}$ , and that the cell potential is  $+1.2272 \text{ V}$ , (a) write the Nernst equation for the cell. Determine (b) the standard cell potential, (c)  $\Delta_f G$ ,  $\Delta_f G^\circ$ , and  $K$  for the cell reaction, (d) the mean ionic activity and activity coefficient of  $\text{ZnCl}_2$  from the measured cell potential, and (e) the mean ionic activity coefficient of  $\text{ZnCl}_2$  from the Debye–Hückel limiting law. (f) Given that  $(\partial E_{\text{cell}}/\partial T)_p = -4.52 \times 10^{-4} \text{ V K}^{-1}$ , calculate  $\Delta_f S$  and  $\Delta_f H$ .

\* Problems denoted with the symbol † were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

**6.17** The potential of the cell  $\text{Pt}|\text{H}_2(\text{g}, p^\circ)|\text{HCl}(\text{aq}, b)|\text{Hg}_2\text{Cl}_2(\text{s})|\text{Hg}(\text{l})$  has been measured with high precision with the following results at 25°C:

$b/(\text{mmol kg}^{-1})$	1.6077	3.0769	5.0403	7.6938	10.9474
$E/\text{V}$	0.60080	0.56825	0.54366	0.52267	0.50532

Determine the standard cell potential and the mean activity coefficient of HCl at these molalities. (Make a least-squares fit of the data to the best straight line.)

**6.18** Careful measurements of the potential of the cell  $\text{Pt}|\text{H}_2(\text{g}, p^\circ)|\text{NaOH}(\text{aq}, 0.0100 \text{ mol kg}^{-1}), \text{NaCl}(\text{aq}, 0.01125 \text{ mol kg}^{-1})|\text{AgCl}(\text{s})|\text{Ag}$  have been reported. Among the data is the following information:

$\theta/^\circ\text{C}$	20.0	25.0	30.0
$E_{\text{cell}}/\text{V}$	1.04774	1.04864	1.04942

Calculate  $pK_w$  at these temperatures and the standard enthalpy and entropy of the autoprotolysis of water at 25.0°C.

**6.19** Measurements of the potential of cells of the type  $\text{Ag}|\text{AgX}(\text{s})|\text{MX}(b_1)|\text{M}_x\text{Hg}|\text{MX}(b_2)|\text{AgX}(\text{s})|\text{Ag}$ , where  $\text{M}_x\text{Hg}$  denotes an amalgam and the electrolyte is LiCl in ethylene glycol, are given below. Estimate the activity coefficient at the concentration marked \* and then use this value to calculate activity coefficients from the measured cell potential at the other concentrations. Base your answer on the following version of the extended Debye–Hückel law:

$$\log \gamma_{\pm} = -\frac{AI^{1/2}}{1 + BI^{1/2}} + CI$$

with  $A = 1.461$ ,  $B = 1.70$ ,  $C = 0.20$ , and  $I = b/b^*$ . For  $b_2 = 0.09141 \text{ mol kg}^{-1}$ :

$b/(\text{mol kg}^{-1})$	0.0555	0.09141*	0.1652	0.2171	1.040	1.350
$E/\text{V}$	-0.0220	0.0000	0.0263	0.0379	0.1156	0.1336

**6.20** The standard potential of the  $\text{AgCl}/\text{Ag}, \text{Cl}^-$  couple fits the expression

$$E^\circ/\text{V} = 0.23659 - 4.8564 \times 10^{-4}(\theta/^\circ\text{C}) - 3.4205 \times 10^{-6}(\theta/^\circ\text{C})^2 + 5.869 \times 10^{-9}(\theta/^\circ\text{C})^3$$

Calculate the standard Gibbs energy and enthalpy of formation of  $\text{Cl}^-(\text{aq})$  and its entropy at 298 K.

**6.21†** The table below summarizes the potential of the cell  $\text{Pd}|\text{H}_2(\text{g}, 1 \text{ bar})|\text{BH}(\text{aq}, b), \text{B}(\text{aq}, b)|\text{AgCl}(\text{s})|\text{Ag}$ . Each measurement is made at equimolar concentrations of 2-aminopyridinium chloride (BH) and 2-aminopyridine (B). The data are for 25°C and it is found that  $E_{\text{cell}}^\circ = 0.22251 \text{ V}$ . Use the data to determine  $pK_a$  for the acid at 25°C and the mean activity coefficient ( $\gamma_{\pm}$ ) of BH as a function of molality ( $b$ ) and ionic strength ( $I$ ). Use the extended Debye–Hückel equation for the mean activity coefficient in the form

$$\log \gamma_{\pm} = -\frac{AI^{1/2}}{1 + BI^{1/2}} + Cb$$

where  $A = 0.5091$  and  $B$  and  $C$  are parameters that depend upon the ions. Draw a graph of the mean activity coefficient with  $b = 0.04 \text{ mol kg}^{-1}$  and  $0 \leq I \leq 0.1$ .

$b/(\text{mol kg}^{-1})$	0.01	0.02	0.03	0.04	0.05
$E_{\text{cell}}(25^\circ\text{C})/\text{V}$	0.74452	0.72853	0.71928	0.71314	0.70809
$b/(\text{mol kg}^{-1})$	0.06	0.07	0.08	0.09	0.10
$E_{\text{cell}}(25^\circ\text{C})/\text{V}$	0.70380	0.70059	0.69790	0.69571	0.69338

*Hint.* Use mathematical software or a spreadsheet.

### Theoretical problems

**6.22** Express the equilibrium constant of a gas-phase reaction  $\text{A} + 3 \text{B} \rightleftharpoons 2 \text{C}$  in terms of the equilibrium value of the extent of reaction,  $\xi$ , given that

initially A and B were present in stoichiometric proportions. Find an expression for  $\xi$  as a function of the total pressure,  $p$ , of the reaction mixture and sketch a graph of the expression obtained.

**6.23** Find an expression for the standard reaction Gibbs energy at a temperature  $T'$  in terms of its value at another temperature  $T$  and the coefficients  $a$ ,  $b$ , and  $c$  in the expression for the molar heat capacity listed in Table 2.2. Evaluate the standard Gibbs energy of formation of  $\text{H}_2\text{O}(\text{l})$  at 372 K from its value at 298 K.

**6.24** Derive an expression for the temperature dependence of  $K_c$  for a gas-phase reaction.

### Applications: to biology, environmental science, and chemical engineering

**6.25** Here we investigate the molecular basis for the observation that the hydrolysis of ATP is exergonic at pH = 7.0 and 310 K. (a) It is thought that the exergonicity of ATP hydrolysis is due in part to the fact that the standard entropies of hydrolysis of polyphosphates are positive. Why would an increase in entropy accompany the hydrolysis of a triphosphate group into a diphosphate and a phosphate group? (b) Under identical conditions, the Gibbs energies of hydrolysis of  $\text{H}_4\text{ATP}$  and  $\text{MgATP}^{2-}$ , a complex between the  $\text{Mg}^{2+}$  ion and  $\text{ATP}^{4-}$ , are less negative than the Gibbs energy of hydrolysis of  $\text{ATP}^{4-}$ . This observation has been used to support the hypothesis that electrostatic repulsion between adjacent phosphate groups is a factor that controls the exergonicity of ATP hydrolysis. Provide a rationale for the hypothesis and discuss how the experimental evidence supports it. Do these electrostatic effects contribute to the  $\Delta_r H$  or  $\Delta_r S$  terms that determine the exergonicity of the reaction? *Hint.* In the  $\text{MgATP}^{2-}$  complex, the  $\text{Mg}^{2+}$  ion and  $\text{ATP}^{4-}$  anion form two bonds: one that involves a negatively charged oxygen belonging to the terminal phosphate group of  $\text{ATP}^{4-}$  and another that involves a negatively charged oxygen belonging to the phosphate group adjacent to the terminal phosphate group of  $\text{ATP}^{4-}$ .

**6.26** To get a sense of the effect of cellular conditions on the ability of ATP to drive biochemical processes, compare the standard Gibbs energy of hydrolysis of ATP to ADP with the reaction Gibbs energy in an environment at 37°C in which pH = 7.0 and the ATP, ADP, and  $\text{P}_i^-$  concentrations are all  $1.0 \mu\text{mol dm}^{-3}$ .

**6.27** Under biochemical standard conditions, aerobic respiration produces approximately 38 molecules of ATP per molecule of glucose that is completely oxidized. (a) What is the percentage efficiency of aerobic respiration under biochemical standard conditions? (b) The following conditions are more likely to be observed in a living cell:  $p_{\text{CO}_2} = 5.3 \times 10^{-2} \text{ atm}$ ,  $p_{\text{O}_2} = 0.132 \text{ atm}$ ,  $[\text{glucose}] = 5.6 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{ATP}] = [\text{ADP}] = [\text{P}_i] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ , pH = 7.4,  $T = 310 \text{ K}$ . Assuming that activities can be replaced by the numerical values of molar concentrations, calculate the efficiency of aerobic respiration under these physiological conditions. (c) A typical diesel engine operates between  $T_c = 873 \text{ K}$  and  $T_h = 1923 \text{ K}$  with an efficiency that is approximately 75 per cent of the theoretical limit of  $(1 - T_c/T_h)$  (see Section 3.2). Compare the efficiency of a typical diesel engine with that of aerobic respiration under typical physiological conditions (see part b). Why is biological energy conversion more or less efficient than energy conversion in a diesel engine?

**6.28** In anaerobic bacteria, the source of carbon may be a molecule other than glucose and the final electron acceptor is some molecule other than  $\text{O}_2$ . Could a bacterium evolve to use the ethanol/nitrate pair instead of the glucose/ $\text{O}_2$  pair as a source of metabolic energy?

**6.29** The standard potentials of proteins are not commonly measured by the methods described in this chapter because proteins often lose their native structure and function when they react on the surfaces of electrodes. In an alternative method, the oxidized protein is allowed to react with an

appropriate electron donor in solution. The standard potential of the protein is then determined from the Nernst equation, the equilibrium concentrations of all species in solution, and the known standard potential of the electron donor. We illustrate this method with the protein cytochrome *c*. The one-electron reaction between cytochrome *c*, cyt, and 2,6-dichloroindophenol, D, can be followed spectrophotometrically because each of the four species in solution has a distinct absorption spectrum. We write the reaction as  $\text{cyt}_{\text{ox}} + \text{D}_{\text{red}} \rightleftharpoons \text{cyt}_{\text{red}} + \text{D}_{\text{ox}}$ , where the subscripts 'ox' and 'red' refer to oxidized and reduced states, respectively. (a) Consider  $E_{\text{cyt}}^\circ$  and  $E_{\text{D}}^\circ$  to be the standard potentials of cytochrome *c* and D, respectively. Show that, at equilibrium, a plot of  $\ln([\text{D}_{\text{ox}}]_{\text{eq}}/[\text{D}_{\text{red}}]_{\text{eq}})$  versus  $\ln([\text{cyt}_{\text{ox}}]_{\text{eq}}/[\text{cyt}_{\text{red}}]_{\text{eq}})$  is linear with slope of 1 and  $y$ -intercept  $F(E_{\text{cyt}}^\circ - E_{\text{D}}^\circ)/RT$ , where equilibrium activities are replaced by the numerical values of equilibrium molar concentrations. (b) The following data were obtained for the reaction between oxidized cytochrome *c* and reduced D in a pH 6.5 buffer at 298 K. The ratios  $[\text{D}_{\text{ox}}]_{\text{eq}}/[\text{D}_{\text{red}}]_{\text{eq}}$  and  $[\text{cyt}_{\text{ox}}]_{\text{eq}}/[\text{cyt}_{\text{red}}]_{\text{eq}}$  were adjusted by titrating a solution containing oxidized cytochrome *c* and reduced D with a solution of sodium ascorbate, which is a strong reductant. From the data and the standard potential of D of 0.237 V, determine the standard potential cytochrome *c* at pH 6.5 and 298 K.

$[\text{D}_{\text{ox}}]_{\text{eq}}/[\text{D}_{\text{red}}]_{\text{eq}}$	0.00279	0.00843	0.0257	0.0497	0.0748	0.238	0.534
$[\text{cyt}_{\text{ox}}]_{\text{eq}}/[\text{cyt}_{\text{red}}]_{\text{eq}}$	0.0106	0.0230	0.0894	0.197	0.335	0.809	1.39

**6.30‡** The dimerization of ClO in the Antarctic winter stratosphere is believed to play an important part in that region's severe seasonal depletion of ozone. The following equilibrium constants are based on measurements on the reaction  $2 \text{ClO}(\text{g}) \rightarrow (\text{ClO})_2(\text{g})$ .

$T/\text{K}$	233	248	258	268	273	280
$K$	$4.13 \times 10^8$	$5.00 \times 10^7$	$1.45 \times 10^7$	$5.37 \times 10^6$	$3.20 \times 10^6$	$9.62 \times 10^5$

$T/\text{K}$	288	295	303
$K$	$4.28 \times 10^5$	$1.67 \times 10^5$	$6.02 \times 10^4$

(a) Derive the values of  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  for this reaction. (b) Compute the standard enthalpy of formation and the standard molar entropy of  $(\text{ClO})_2$  given  $\Delta_f H^\circ(\text{ClO}) = +101.8 \text{ kJ mol}^{-1}$  and  $S_m^\circ(\text{ClO}) = 266.6 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**6.31‡** Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions that bring about the Antarctic ozone hole. Standard reaction Gibbs energies are as follows:

- (i)  $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{s})$   $\Delta_r G^\circ = -23.6 \text{ kJ mol}^{-1}$
- (ii)  $\text{H}_2\text{O}(\text{g}) + \text{HNO}_3(\text{g}) \rightarrow \text{HNO}_3 \cdot \text{H}_2\text{O}(\text{s})$   $\Delta_r G^\circ = -57.2 \text{ kJ mol}^{-1}$
- (iii)  $2 \text{H}_2\text{O}(\text{g}) + \text{HNO}_3(\text{g}) \rightarrow \text{HNO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$   $\Delta_r G^\circ = -85.6 \text{ kJ mol}^{-1}$
- (iv)  $3 \text{H}_2\text{O}(\text{g}) + \text{HNO}_3(\text{g}) \rightarrow \text{HNO}_3 \cdot 3\text{H}_2\text{O}(\text{s})$   $\Delta_r G^\circ = -112.8 \text{ kJ mol}^{-1}$

Which solid is thermodynamically most stable at 190 K if  $p_{\text{H}_2\text{O}} = 1.3 \times 10^{-7} \text{ bar}$  and  $p_{\text{HNO}_3} = 4.1 \times 10^{-10} \text{ bar}$ ? *Hint.* Try computing  $\Delta_r G$  for each reaction under the prevailing conditions; if more than one solid forms spontaneously, examine  $\Delta_r G$  for the conversion of one solid to another.

**6.32‡** Suppose that an iron catalyst at a particular manufacturing plant produces ammonia in the most cost-effective manner at 450°C when the pressure is such that  $\Delta_r G$  for the reaction  $\frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g})$  is equal to  $-500 \text{ J mol}^{-1}$ . (a) What pressure is needed? (b) Now suppose that a new catalyst is developed that is most cost-effective at 400°C when the pressure gives the same value of  $\Delta_r G$ . What pressure is needed when the new catalyst is used? What are the advantages of the new catalyst? Assume that (i) all gases are perfect gases or that (ii) all gases are van der Waals gases. Isotherms of  $\Delta_r G(T, p)$  in the pressure range  $100 \text{ atm} \leq p \leq 400 \text{ atm}$  are needed to derive the answer. (c) Do the isotherms you plotted confirm Le Chatelier's principle concerning the response of equilibrium changes in temperature and pressure?