## Thermodynamics **AP Problems**

## **Practice Exercises**

## Multiple-Choice

For the first four problems below, one or more of the following responses will apply; each response may be used more than once or not at all in these questions.

- I. ΔG°
- II. ΔS°
- III. ΔH°
- IV. ΔG
- V. H
- 1. Which of these must be negative for a reaction to be spontaneous?
  - (A) I
  - (B) III
  - (C) I, II, and IV (CE)
  - (D) IV
  - (E) I, III, and V

- 2. Which of these cannot be determined?
  - (A) I and III
  - (B) II
  - (C) I, II, and IV
  - (D) I, III, and IV
  - (E) V
- 3. Which of these are extensive values?
  - (A) I and III
  - (B) II
  - (C) I, II, and IV
  - (D) IV, and V
  - (E) I, III, and V

- 4. If \_\_\_\_ is negative and 8. Which of the following explains is positive, a reaction will never be spontaneous.
  - (A) II, III
  - (B) III, IV
  - (C) I, II
  - (D) IV, III
  - (E) I, V
- 5. When 0.400 g of CH<sub>4</sub> is burned in excess oxygen in a bomb calorimeter that has a heat capacity of 3245 J  $^{\circ}$ C<sup>-1</sup>, a temperature increase of 6.795°C is observed. What is the value of  $q_{\nu}$ ?
  - (A)  $220 \text{ kJ mol}^{-1}$
  - (B) -882 kJ
  - (C) 477 kJ
  - (D) -22.05 kJ
  - (E)  $8.820 \text{ kJ g}^{-1}$
- 6. Using the data in question 1, determine  $\Delta H^{\circ}$  for the combustion of methane.
  - (A)  $-22.05 \text{ kJ mol}^{-1}$
  - (B) -882 kJ
  - (C) +22.05 kJ
  - (D)  $-8.820 \text{ kJ g}^{-1}$
  - (E) This value cannot be determined because w is not known.
- 7. Which of the following describes a system that CANNOT be spontaneous?
  - (A)  $\Delta H^{\circ}$  is positive, and  $\Delta S^{\circ}$  is negative.
  - (B)  $\Delta H^{\circ}$  is positive, and  $\Delta S^{\circ}$  is positive.
  - (C)  $\Delta H^{\circ}$  is negative, and  $\Delta S^{\circ}$  is negative.
  - (D)  $\Delta H^{\circ}$  is negative, and  $\Delta S^{\circ}$  is positive.
  - (E)  $\Delta H^{\circ}$  is 0.00, and  $\Delta S^{\circ}$  is positive.

- the fact that, when KCl is dissolved, water condenses on the outside of the beaker?
  - (A)  $\Delta H^{\circ}$  is positive, and  $\Delta S^{\circ}$  is negative.
  - (B)  $\Delta H^{\circ}$  is positive, and  $\Delta S^{\circ}$  is positive.
  - (C)  $\Delta H^{\circ}$  is negative, and  $\Delta S^{\circ}$  is negative.
  - (D)  $\Delta H^{\circ}$  is negative, and  $\Delta S^{\circ}$  is positive.
  - (E)  $\Delta H^{\circ}$  is 0.00, and  $\Delta S^{\circ}$  is negative.
- 9. The reaction with the greatest expected entropy decrease is
  - (A)  $CH_4(g)$  $2O_2(g)$  $CO_2(g)$  $2H_2O(g)$
  - (B)  $CH_4(\ell)$  $2O_{2}(g)$  $CO_2(g)$  $2H_2O(g)$
  - (C)  $CH_4(g)$  $2O_2(g)$  $CO_2(g)$  $2H_2O(\ell)$
  - (D)  $CH_4(g)$  $2O_{2}(g)$  $CO_2(s)$  $2H_2O(g)$
  - (E)  $CH_4(\ell)$  $2O_{2}(g)$  $CO_2(g)$ dd<del>+</del>q  $2H_2O(\ell)$
- 10. Water boils at 100°C with a molar heat of vaporization of +43.9 kJ. What is the entropy change when

$$H_2O(g) \rightarrow H_2O(\ell)$$

at 100°C?

- (A) Problem cannot be solved;  $\Delta G^{\circ}$  must also be known.
- (B) Problem cannot be solved; this is not a chemical reaction.
- (C)  $-439 \text{ J K}^{-1}$
- (D) +0.439 J K<sup>-1</sup>
- (E)  $-118 \text{ J K}^{-1}$

- 11. The Dulong and Petit law says that 14. Which of the following is the the molar specific heat of solid elements is approximately 25 J mol<sup>-1</sup> K<sup>-1</sup>. This suggests that
  - (A) the heat absorbed depends only on the number of atoms
  - (B) the heat absorbed depends on the volume change with temperature
  - (C) the heat absorbed can be calculated from the first law of thermodynamics
  - (D) potential energy and heat energy are inversely related
  - (E) This law is an oddity since it does not apply to elements that are liquids or gases.
- 12. A gas is allowed to expand from an initial volume of 5.00 L and pressure of 3.00 atm to a volume of 15.0 L and pressure of 1.00 atm. What is the value of w?
  - (A)  $+30.0 \, \text{L}$  atm
  - (B)  $+10.0 \, \text{L}$  atm
  - (C) -45.0 L atm
  - (D) +15.0 L atm
  - (E) -10.0 L atm
- 13. In question 8 the units of work are given as L atm. To convert L atm to the metric unit of joules, we need to know
  - (A) Avogadro's constant and Planck's constant
  - (B) the universal gas law constant in units of L atm mol<sup>-1</sup> K<sup>-1</sup>
  - (C) the universal gas law constant in units of J mol<sup>-1</sup> K<sup>-1</sup>
  - (D) both B and C
  - (E) A, B, and C

- LEAST probable for a combustion reaction?
  - (A)  $\Delta G^{\circ}$  is a large negative number.
  - (B)  $\Delta S^{\circ}$  is a large negative number.
  - (C)  $\Delta H^{\circ}$  is a large negative number.
  - (D)  $K_{eq}$  is a large positive number.
  - (E) Q, the reaction quotient, is a small number.
- 15. Of the following, which can be precisely determined for a chemical substance?
  - (A) entropy, S
  - (B) enthalpy, H
  - (C) free energy, G
  - (D) internal energy, E
  - (E) all of these
- 16. The heat of formation of  $CH_3OH(\ell) = -238.6 \text{ kJ mol}^{-1}$ of  $CO_2(g) = -393.5 \text{ kJ mol}^{-1}$ , and of  $H_2O(g) = -241.8 \text{ kJ}$  $\text{mol}^{-1}$ . What is  $\Delta H^{\circ}$  for the heat of combustion of methanol?
  - (A) -396.7 kJ
  - (B) -1277 kJ
  - (C) -638.5 kJ
  - (D) + 396.7 kJ
  - (E) This value cannot be calculated without the heat of formation for  $O_2(g)$ .
- 17. The rate of reaction will be large if
  - (A)  $\Delta G^{\circ}$  is a large negative number
  - (B)  $\Delta S^{\circ}$  is a large negative number
  - (C)  $\Delta H^{\circ}$  is a large negative number
  - (D)  $K_{eq}$  is a large positive number
  - (E) None of the above can be used to estimate reaction rates.

18. Given the following thermochemical data:

$$N_2O_4(g) \rightarrow 2NO_2(g)$$
  $\Delta H^{\circ} = +57.93 \text{ kJ}$   
 $2NO(g) + O_2(g) \rightarrow 2NO_2(g) \Delta H^{\circ} = -113.14 \text{ kJ}$ 

determine the heat of the reaction

$$2NO(g) + O_2(g) \rightarrow N_2O_4(g)$$

- (A) 171.07 kJ
- (B) -55.21 kJ
- (C) -171.07 kJ
- (D) + 55.21 kJ
- (E) 85.54 kJ
- 19. Which of the following can change the value of  $\Delta G^{\circ}$  for a chemical reaction?
  - (A) changes in the total pressure
  - (B) changes in the pressures of the reactants
  - (C) changes in the concentrations of the reactants
  - (D) changes in the temperature in
  - (E) the presence of a catalyst
- 20. At what temperature is  $K_{eq} = 1.00$ if  $\Delta S^{\circ} = 22.6 \text{ J K}^{-1}$  and  $\Delta H^{\circ} =$ 15.3 kJ for a chemical reaction?
  - (A) 404°C
  - (B) 677°C
  - (C) 0.67°C
  - (D) 1477°C
  - (E) 1204°C
- 22. The reaction

$$2SO_3(g) \rightarrow 2S(s) + 3O_2(g)$$

at 25°C.

- (A) + 396 kJ
- (B) -446 kJ
- (C) + 346 kJ
- (D) -346 kJ
- (E) +742 kJ

$$2C_6H_6(\ell) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(\ell)$$

is expected to have

- (A) a positive  $\Delta H$  and a negative  $\Delta S$
- (B) a negative  $\Delta H$  and a negative  $\Delta S$
- (C) a positive  $\Delta H$  and a positive  $\Delta S$
- (D) a negative  $\Delta H$  and a negative  $\Delta S$
- (E) These predictions cannot be made.

- 23. The evaporation of any liquid is expected to have
  - (A) a positive  $\Delta H$  and a negative
  - (B) a negative  $\Delta H$  and a negative
  - (C) a positive  $\Delta H$  and a positive
  - (D) a positive  $\Delta H$  and a negative
  - (E) These predictions cannot be

- 24. Which of the following is most likely to be true?
  - (A) No products are formed in a nonspontaneous reaction.
  - (B) A positive  $\Delta G^{\circ}$  indicates a spontaneous reaction.
  - (C) A positive  $\Delta S^{\circ}$  always means that the reaction is spontaneous.
  - (D) A spontaneous reaction always goes to completion.
  - (E) Combustion of organic compounds has a negative  $\Delta H^{\circ}$ .

See Appendix 1 for explanations of answers.

## Free-Response

Answer the following questions using the concepts of thermodynamics and equilibrium and the methods for solving problems.

- What parameters define whether or not a given reaction is spontaneous? Based on those parameters, what does it mean to say a reaction is spontaneous?
- (b) What is the difference between E,  $\Delta E$ , and  $\Delta E^{\circ}$ ?
- (c) Tables of thermodynamic data list heat of formation,  $\Delta H_f^{\circ}$ , standard free energy,  $\Delta G_{298}^{\circ}$ , and entropy, S°. Why don't entropy values have a delta symbol,  $\Delta$ ? What other difference does a table of entropy values have?

- (d) The value of  $K_c$  for the reaction 2NO + O<sub>2</sub>  $\leftrightarrows$  N<sub>2</sub>O<sub>4</sub> is 36 at a certain temperature. Calculate K for the following reactions.
  - (i)  $6NO + 3O_2 \leftrightarrows 3N_2O_4$ (ii)  $NO + \frac{1}{2}O_2 \leftrightarrows \frac{1}{2}N_2O_4$ (iii)  $2N_2O_4 \leftrightarrows 4NO + 2O_2$