

## 5.E: The Second Law (Exercises)

### Q5.1

What is the minimum amount of work needed to remove 10.0 J of energy from a freezer at  $-10.0\text{ }^{\circ}\text{C}$ , depositing the energy into a room that is  $22.4\text{ }^{\circ}\text{C}$ ?

### Q5.2

Consider the isothermal, reversible expansion of 1.00 mol of a monatomic ideal gas ( $C_V = 3/2 R$ ) from 10.0 L to 25.0 L at 298 K. Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ , and  $\Delta S$  for the expansion.

### Q5.3

Consider the isobaric, reversible expansion of 1.00 mol of a monatomic ideal gas ( $C_p = 5/2 R$ ) from 10.0 L to 25.0 L at 1.00 atm. Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ , and  $\Delta S$  for the expansion.

### Q5.4

Consider the isochoric, reversible temperature increase of 1.00 mol of a monatomic ideal gas ( $C_V = 3/2 R$ ) occupying 25.0 L from 298 K to 345 K. Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ , and  $\Delta S$  for this process.

### Q5.5

Consider the adiabatic expansion of 1.00 mol of a monatomic ideal gas ( $C_V = 3/2 R$ ) from 10.0 L at 273 K to a final volume of 45.0 L. Calculate  $\Delta T$ ,  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ , and  $\Delta S$  for the expansion.

### Q5.6

15.0 g of ice ( $\Delta H_{fus} = 6.009\text{ kJ/mol}$ ) at  $0\text{ }^{\circ}\text{C}$  sits in a room that is at  $21\text{ }^{\circ}\text{C}$ . The ice melts to form liquid at  $0\text{ }^{\circ}\text{C}$ . Calculate the entropy change for the ice, the room, and the universe. Which has the largest magnitude?

### Q5.7

15.0 g of liquid water ( $C_p = 75.38\text{ J mol}^{-1}\text{ }^{\circ}\text{C}^{-1}$ ) at  $0\text{ }^{\circ}\text{C}$  sits in a room that is at  $21\text{ }^{\circ}\text{C}$ . The liquid warms from  $0\text{ }^{\circ}\text{C}$  to  $21\text{ }^{\circ}\text{C}$ . Calculate the entropy change for the liquid, the room, and the universe. Which has the largest magnitude?

### Q5.8

Calculate the entropy change for taking 12.0 g of  $\text{H}_2\text{O}$  from the solid phase ( $C_p = 36.9\text{ J mol}^{-1}\text{ K}^{-1}$ ) at  $-12.0\text{ }^{\circ}\text{C}$  to liquid ( $C_p = 75.2\text{ J mol}^{-1}\text{ K}^{-1}$ ) at  $13.0\text{ }^{\circ}\text{C}$ . The enthalpy of fusion for water is  $\Delta H_{fus} = 6.009\text{ kJ/mol}$ .

### Q5.9

Using Table T1, calculate the standard reaction entropies ( $\Delta S^{\circ}$ ) for the following reactions at 298 K.

- $\text{CH}_3\text{CH}_2\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$
- $\text{C}_{12}\text{H}_{22}\text{O}_{11}(s) + 12\text{O}_2 \rightarrow 12\text{CO}_2(g) + 11\text{H}_2\text{O}(l)$
- $2\text{POCl}_3(l) \rightarrow 2\text{PCl}_3(l) + \text{O}_2(g)$
- $2\text{KBr}(s) + \text{Cl}_2(g) \rightarrow 2\text{KCl}(s) + \text{Br}_2(l)$
- $\text{SiH}_4(g) + 2\text{Cl}(g) \rightarrow \text{SiCl}_4(l) + 2\text{H}_2(g)$

### Q5.10

1.00 mole of an ideal gas is taken through a cyclic process involving three steps:

- Isothermal expansion from  $V_1$  to  $V_2$  at  $T_1$
- Isochoric heating from,  $T_1$  to  $T_2$  at  $V_2$
- Adiabatic compression from  $V_2$  to  $V_1$

- Graph the process on a V-T diagram.
- Find  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta S$  for each leg. (If you want, you can find  $\Delta H$  too!)

- c. Use the fact that  $\Delta S$  for the entire cycle must be zero (entropy being a state function and all ...), determine the relationship between  $V_1$  and  $V_2$  in terms of  $C_v$ ,  $T_1$  and  $T_2$ .

### Q5.11

2.00 moles of a monatomic ideal gas ( $C_v = 3/2 R$ ) initially exert a pressure of 1.00 atm at 300.0 K. The gas undergoes the following three steps, all of which are reversible:

- I. isothermal compression to a final pressure of 2.00 atm,
- II. Isobaric temperature increase to a final temperature of 400.0 K, and
- III. A return to the initial state along a pathway in which

$$p = a + bT \quad (5.E.1)$$

where  $a$  and  $b$  are constants. Sketch the cycle on a pressure-temperature plot, and calculate  $\Delta U$  and  $\Delta S$  for each of the legs. Are  $\Delta U$  and  $\Delta S$  zero for the sum of the three legs?

### Q5.12

A 10.0 g piece of iron ( $C = 0.443 \text{ J/g } ^\circ\text{C}$ ) initially at  $97.6^\circ\text{C}$  is placed in 50.0 g of water ( $C = 4.184 \text{ J/g } ^\circ\text{C}$ ) initially at  $22.3^\circ\text{C}$  in an insulated container. The system is then allowed to come to thermal equilibrium. Assuming no heat flow to or from the surroundings, calculate

- a. the final temperature of the metal and water
- b. the change in entropy for the metal
- c. the change in entropy for the water
- d. the change in entropy for the universe

### Q5.13

Consider a crystal of  $\text{CHFCIBr}$  as having four energetically equivalent orientations for each molecule. What is the expected residual entropy at 0 K for 2.50 mol of the substance?

### Q5.14

A sample of a certain solid is measured to have a constant pressure heat capacity of  $0.436 \text{ J mol}^{-1} \text{ K}^{-1}$  at 10.0 K. Assuming the Debye extrapolation model

$$C_p(T) = aT^3 \quad (5.E.2)$$

holds at low temperatures, calculate the molar entropy of the substance at 12.0 K.

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