Thermochemistry

Answers and Explanations

1. A

A thermodynamic system has two means of exchanging energy with its surroundings, heat flow and pressure-volume work. Heat flow, Q, is the transfer of thermal energy due to temperature difference. Work, W, is macroscopic energy transfer between the system and its surroundings that occurs through force exerted along the direction of a displacement. In a thermodynamic system, work manifests as the exertion of pressure through a change in volume. The First Law of Thermodynamics expresses the principle of energy conservation for thermodynamic systems. The total internal energy change of the system can be determined as an accounting of the heat flow and the work.

$$\begin{aligned}\Delta U &= Q - W\\ &= Q - P^{*}\Delta V\end{aligned}$$

ΔU = internal energy change
Q = heat flow
W = macroscopic work

P^{*} = constant pressure
ΔV = volume change

Heat flowing from the system into the surroundings costs the system internal energy, so the system lost 500 kJ of internal energy due to the heat flow. Additionally, expansion, in which the system performs pressure-volume work on the surroundings, also costs the system. It loses an additional 250 kJ of energy due to the thermodynamic work.

2. C

One calorie is the amount of heat required to increase the temperature of 1 g of water by 1°C. One calorie equals 4.18 J.

$$1 \text{ calorie} = 4.18 \text{ joules}$$

3. A

The specific heat tells you how many joules (or calories) of heat flow are required to raise a *gram* of a substance by one degree. The molar heat capacity tells you the heat flow to raise a *mole* of a substance by one degree. It's not difficult to see then that one would multiply specific heat by molecular weight to convert it to molar heat capacity. For the purpose of our problem then we could do this in reverse and divide the molar heat capacity by the specific heat to determine molecular weight.

$$\frac{25\ \text{J K}^{-1}\ \text{mol}^{-1}}{0.20\ \text{J K}^{-1}\ \text{g}^{-1}} = 125\ \text{g mol}^{-1}$$

4. D

As long as pressure is constant, any change in the enthalpy of a system will equal the heat flow, so a positive enthalpy change means that heat is absorbed by the system. The concept of the equivalence of enthalpy change and heat flow (as long as pressure is constant) is the foundation of thermochemistry. It allows us to describe heat flow in terms of the change in a state function. Enthalpy change is path independent.

Note with regard to choice 'B' that enthalpy change equals internal energy change only if the volume of the system remains constant (and thus no thermodynamic work is performed).

5. B

The heat flow to or from an object changing temperature equals the product of the mass of the object, the specific heat of its material, and the temperature change.

$$Q = m\,c\,\Delta T$$

The amount of heat flowing from the alloy will equal the heat flowing into the water.

$$(20\ \text{g})\ c\ (80^{\circ}\text{C} - 30^{\circ}\text{C}) = (100\ \text{g})(1\ \text{cal g}^{-1}\ {}^{\circ}\text{C}^{-1})(30^{\circ}\text{C} - 28^{\circ}\text{C})$$

$$(20\ \text{g})\ c\ (80^{\circ}\text{C} - 30^{\circ}\text{C}) = 200\ \text{cal}$$

$$c = 0.2\ \text{cal g}^{-1}\ {}^{\circ}\text{C}^{-1}$$

6. B

For all but methane, the elements are listed in their standard states. They are thus assigned a value of zero for standard enthalpy of formation. There is no heat flow involved in the formation of these from their standard states because they are the standard states!

7. B

In our reaction vessel, we start with approximately ¾ of a mole of carbon. We react this with a bit more than ½ of a mole of O_2. However, the stoichiometry of the reaction calls for a 1:1 ratio for both reagents to be completely consumed, so O_2 is going to be a limiting reagent in this case, dictating the amount of CO_2 formed. In other words, using mental math, we see we only form somewhat more than half a mole of CO_2. Because we are forming somewhat more than half a mole of CO_2, the 226 kJ liberated represents somewhat more than half of the standard enthalpy of formation of CO_2, which must be 393 kJ mol^{-1}, the only value somewhat less than twice 226 kJ.

8. B

Hess' Law allows us to model the reaction of carbon monoxide with oxygen to form carbon dioxide. We can utilize the given reactions in the problem to construct an imaginary pathway. First, we run the CO formation reaction in reverse ($\Delta H = +110.5$ kJ) to convert a mole of carbon monoxide into graphite and oxygen. We can then react the graphite and oxygen to form a mole of CO_2 ($\Delta H = -393.5$ kJ).

9. B

When our reaction at stoichiometric values has gone to completion, the system will have changed from 3 moles of gas to 2 moles of gas. The volume decreased. Therefore, the system is losing enthalpy in the pressure-volume product in addition to the loss of internal energy ($H = U + PV$). From the point of view of the first law of thermodynamics, the surroundings are performing work on the system as it compresses which adds to the thermal energy from the internal energy decrease that then flows out. Therefore, the enthalpy decrease (heat flow) is greater than the internal energy decrease.

10. C

The standard enthalpy of formation of a compound represents the enthalpy change involved in forming that compound from its constituent elements in their standard states. The standard state of an element is the agreed upon most common pure form of the element. For example, the standard state of oxygen is O_2 gas. The standard state of carbon is C(graphite). Using standard enthalpies of formation to compute the enthalpy change of a reaction is a useful technique in thermochemistry because the standard enthalpy of formation of almost every compound of interest will have been experimentally determined and recorded. This allows us to construct an imaginary path from the reagents to the products in which we transform the reagents into the standard states (heat flow occurring of minus the standard enthalpy of formation of the reagents) and then form the products (heat flow occurring equal to the standard enthalpy of formation of the products). For a particular reaction you scale the standard enthalpies to reflect the stoichiometry of the reaction. We know that the enthalpy computed in this way will be valid because the enthalpy change doesn't depend on the path (Hess' Law).

11. A

Hess' law states that the total enthalpy change during the complete course of a chemical reaction is the same whether the reaction is made in one step or in several steps. The law is valid because the enthalpy of a chemical system is a state function of the system, so the difference in enthalpy between two states depends on those states, not on the path between the states. This is a fundamental idea of chemical thermodynamics.

Sometimes people say that Hess' Law is that the enthalpy of a reaction equals the standard enthalpy of formation of the products minus the standard enthalpy of formation of the reagents. That isn't Hess' Law, just an important application. Computing the enthalpy change of a reaction in this manner, taking standard enthalpies from a table, is to imagine a stepwise path for the reaction where we have converted the reagents into the standard states of the elements and then converted the standard states into the products. Hess' Law tells us that the enthalpy change we compute will be valid even though the path is imaginary.

12. D

Remember that the enthalpy of a system is the sum of the internal energy and the pressure-volume product.

$$H = U + PV$$

If the pressure is constant, a change in the enthalpy will equal the heat flow. This is what makes enthalpy useful. It can be helpful to think of the enthalpy as the 'thermal potential' of the system, the things in the system that can change and produce heat flow. The internal energy might decrease and lead to heat flow out of the system, or the system might be compressed, leading to heat flow out. You see the same thing in the 1st law of thermodynamics where the heat flow might be the result of internal energy change or thermodynamic work.

$$Q = \Delta U + W$$

In other words, whether the heat flow (Q or ΔH) will equal the internal energy change ΔU will depend on whether or not thermodynamic work is occurring. If the volume of the system is changing, the heat flow and the internal energy change will not be equal. Of the choices presented, all except for vaporization are occurring at constant or approximately constant volume, but to vaporize a mole of water it must expand from 18ml in volume (the volume of 18g of liquid water) to approximately 30L in volume (the volume of 1 mole of gas at 100°C). This takes work equal to the change in volume times atmospheric pressure. This work will represent the amount that the heat of vaporization is greater than the internal energy increase of the water.

13. B

Bond energies can give a good estimate of the enthalpy of a reaction. Imagine breaking the reagent bonds (endothermic) to yield two moles each of loose hydrogen and bromine atoms. This requires input of +435 kJ/mol for H_2 and +192 kJ/mol for the Br_2. Now imagine letting the loose hydrogen and bromine atoms fall together to form two moles of HBr molecules (exothermic). Forming the new bonds would liberate 2 × −368 kJ/mol. The net enthalpy change for our imaginary pathway would be −109 kJ/mol.

14. B

The ideal gas law gives us a straightforward path to the answer. (You really should know the ideal gas constant in these two forms, ie. 8.3 J mol^{-1} K^{-1} and .082 L-atm mol^{-1} K^{-1}.)

$$PV = nRT \qquad P = \frac{nRT}{V}$$

$$P = \frac{(0.3\text{ mol})\,(0.08\text{ L atm mol}^{-1}\text{K}^{-1})\,(298\text{ K})}{(0.5\text{ L})}$$

$$P = 14.3\text{ atm}$$

15. C

The heat flow that occurred is simply the product of the heat capacity of the water bath and apparatus and the temperature change (ΔT = 26.25°C − 25.00°C = 1.25°C). Remember to convert to joules!

$$Q = (10850\text{ cal/°C})(1.25\text{°C}) = 13560\text{ cal}$$

$$(14720\text{ cal})(4.18\text{ J/cal}) = 56700\text{ J}$$

16. C

Choice '**A**' is incorrect. The heat flow occurring here does not equal the enthalpy change for the reaction. Enthalpy ($H = U + PV$) is a state function whose change will equal the heat flow, Q, *only if constant pressure is maintained*. This is one of the reasons so many chemistry problems have the statement 'the reaction was carried out at STP . . .' Constant pressure is necessary for ΔH to equal the heat flow. Choice '**D**' is not correct for the same reason. Bond dissociation energy is the enthalpy change in bond formation under standard conditions. Choice '**C**' is correct because the bomb has a *fixed volume*. There is no thermodynamic work involved, so by the 1st law of thermodynamics the magnitude of heat flow will exactly equal the magnitude of internal energy change.

$$\Delta U = Q - W$$
$$W = 0$$
$$\Delta U = Q$$