Chapter 7: Chemical Energetics

Review Questions

1. Why do standard reference values for temperature and pressure have to be selected when we consider and compare heats of reaction for various reactions? What are the values for the standard temperature and standard pressure?

Solution

Since the heats of reaction will in general depend on temperature and pressure, we need some standard set of values for temperature and pressure so that comparisons of various heats of reaction are made under identical conditions. The standard temperature is 25°C, slightly above room temperature, and the standard pressure is 1 atmosphere.

2. What distinguishes a thermochemical equation from an ordinary chemical equation?

Solution

A thermochemical equation contains the value for the associated ΔH.

3. Why are fractional coefficients permitted in a balanced thermochemical equation? If a formula in a thermochemical equation has a coefficient of (1/2), what does it signify?

Solution

Fractional coefficients are permitted because thermochemical properties are extensive (they depend on the amount of material present). If 1/2 the amount of materials reacts, 1/2 the amount of heat will be generated or required. The coefficients of thermochemical equations are moles of substance.

4. What two conditions must be met by a thermochemical equation so that its standard enthalpy change can be given the symbol ΔH°_{f}?

Solution

The reaction must

(a) produce 1 mol of a compound at 25 °C and 1 atm, and

(b) the reactants must be elements in their standard states.

5. Calculate $\Delta H°$ in kilojoules for the following reaction, the preparation of the unstable acid nitrous acid, HNO_2:

$HCl(g) + NaNO_2(s) \rightarrow HNO_2\ (l) + NaCl(s)$

Use the following thermochemical equations.

$2NaCl(s) + H_2O(l) \rightarrow 2HCl(g) + Na_2O(s)$; $\Delta H° = +507.31$ kJ

$NO(g) + NO_2(g) + Na_2O(s) \rightarrow 2NaNO_2(s)$; $\Delta H° = -427.14$ kJ

$NO(g) + NO_2(g) \rightarrow N_2O(g) + O2\ (g)$; $\Delta H° = -42.68$ kJ

$2HNO_2(l) \rightarrow N_2O(g) + O_2(g) + H_2O(l)$; $\Delta H° = +34.35$ kJ

Solution

If we label the four known thermochemical equations consecutively, 1, 2, 3, and 4, then the sum is made in the following way: Divide Eq. (3) by two, and reverse all of the other Eqs. (1, 2, and 4), while also dividing each by two, we get

$\frac{1}{2} Na_2O(s) + HCl(g) \rightarrow \frac{1}{2} H_2O(l) + NaCl(s)$, $\Delta H° = -253.66$ kJ

$NaNO_2(s) \rightarrow \frac{1}{2} Na_2O(s) + \frac{1}{2} NO_2(g) + \frac{1}{2} NO(g)$, $\Delta H° = +213.57$ kJ

$\frac{1}{2} NO(g) + \frac{1}{2} NO_2(g) \rightarrow \frac{1}{2} N_2O(g) + \frac{1}{2} O_2(g)$, $\Delta H° = -21.34$ kJ

$\frac{1}{2} H_2O(l) + \frac{1}{2} O_2(g) + \frac{1}{2} N_2O(g) \rightarrow HNO_2(l)$, $\Delta H° = -17.18$ kJ

Adding gives:

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$HCl(g) + NaNO_2(s) \rightarrow HNO_2(l) + NaCl(s)$, $\Delta H° = -78.61$ kJ

6. Which quantities in the statement of the first law are state functions and which are not?
Solution

A state function is a thermodynamic quantity whose value is determined only by the state of the system currently, and is not by the system's prior condition or history. A change in a state function is the same regardless of the path that is used to arrive at the final state from the initial state. That is, changes in state function quantities are path-independent. In the statement of the first law, only ΔU is a state function.

7. What are the units of $p\Delta V$ if pressure is expressed in Pascals and volume is expressed in cubic meters?
Solution
A pressure in Pascals, by definition, has the units Newtons m^{-2}, or N m^{-2}.

Thus, p in Pascals times ΔV in m^3 is: N $m^{-2} \times m^3$ = N · m

The last result is the Newton meter, or a force times a distance. By definition, a force of 1 N operating over a distance of 1 meter is the quantity 1 joule. Thus, the quantity $p \times \Delta V$ has the units of energy, namely joules.

8. Which of the following changes is accompanied by the most negative value of ΔU?
(a) A spring is compressed and heated. (b) A compressed spring expands and is cooled.
(c) A spring is compressed and cooled. (d) A compressed spring expands and is heated.
Solution
The most negative value of ΔE will have the most energy released.

(a) Compressing the spring: energy is added to the system: $w > 0$
Heating the spring: energy is added to the system: $q > 0$

(b) Expanding the spring: energy is removed from the system: $w < 0$
Cooling the spring: energy is removed from the system: $q < 0$

(c) Compressing the spring: energy is added to the system: $w > 0$
Cooling the spring: energy is removed from the system: $q < 0$

(d) Expanding the spring: energy is removed from the system: $w < 0$
Heating the spring: energy is added to the system: $q > 0$

In case (b), $q < 0$ and $w < 0$; so, ΔE is the most negative.

9. At constant pressure, what role does the enthalpy change play in determining the spontaneity of an event?
Solution
A change that is characterized by a negative value for ΔH tends to be spontaneous. The only situation where this is not true is that in which the value of the product $T\Delta S$ is sufficiently negative to make the quantity $\Delta G = \Delta H - T\Delta S$ become positive.

10. How do the probabilities of the initial and final states in a process affect the spontaneity of the process?
Solution
Spontaneous processes tend to proceed from states of low probability to states of higher probability.

11. How is the entropy of a substance affected by (a) an increase in temperature, (b) a decrease in volume, (c) changing from a liquid to a solid, and (d) dissociating into individual atoms?
Solution
Entropy is a measure of the randomness of a system, an increase in randomness corresponds to an

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increase in entropy.

(a) An increase in temperature allows the atoms and molecules to move more rapidly; therefore, there is an increase in entropy.
(b) A decrease in volume limits the space that the molecules and atoms have to move in; therefore, there is a decrease in entropy.
(c) Changing a liquid to a solid limits the motion of the molecules; therefore, there is a decrease in entropy.
(d) Dissociating into individual atoms increases the entropy because there are more particles.

12. An instant cold pack purchased in a pharmacy contains a packet of solid ammonium nitrate surrounded by a pouch of water. When the packet of NH_4NO_3 is broken, the solid dissolves in water and a cooling of the mixture occurs because the solution process for NH_4NO_3 in water is endothermic. Explain, in terms of what happens to the molecules and ions, why this mixing occurs spontaneously.

Solution

The ammonium and nitrate atoms are in a highly ordered geometry in the crystalline NH_4NO_3 sample. When NH_4NO_3 dissolves, the NH_4^+ and NO_3^- ions become randomly dispersed throughout the solvent. The increase in randomness that attends the dissolving of the solid is responsible for the process being favorable, or spontaneous, in spite of the fact that the enthalpy change is endothermic.

13. Would you expect the entropy of an alloy (a solution of two metals) to be zero at 0 K? Explain your answer.

Solution

The entropy of a mixture must be higher than that of two separate pure materials, because the mixture is guaranteed to have a higher degree of disorder. Said another way, a mixture is more disordered than either of its two separate components. Only a pure substance can have an entropy of zero, and then only at 0 K.

14. When glucose is oxidized by the body to generate energy, part of the energy is used to make molecules of ATP (adenosine triphosphate). However, of the total energy released in the oxidation of glucose, only 38% actually goes to making ATP. What happens to the rest of the energy?

Solution

As with other processes that are not carried out in a reversible fashion, the energy is lost to the environment and becomes unavailable for use. In addition, much of the energy is lost as heat, which is used to maintain our body temperature.

15. When a warm object is placed in contact with a cold one, they both gradually come to the same temperature. On a molecular level, explain how this is related to entropy and spontaneity.

Solution

Before the heat transfer, the molecules in the hot object vibrate and move more violently than do those of the cooler object. When in contact with one another, the objects transfer heat through collisions, and eventually, some of the kinetic energy of the molecules in the hot object is transferred to the molecules of the cool object. This process of energy transfer continues until the objects have the same temperature. The heat transfer is spontaneous because the scattering of kinetic energy among the molecules of both objects is a process with a positive value for its associated ΔS.

16. Considering the fact that the formation of a bond between two atoms is exothermic and is accompanied by an entropy decrease, explain why all chemical compounds decompose into individual atoms if heated to a high enough temperature.

Solution

The process of bond breaking always has an associated value for ΔH that is positive. Also, since bond

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breaking increases disorder, it always has an associated value for ΔS that is positive. A process such as this, with a positive value for ΔH and a positive value for ΔS, becomes spontaneous at high temperatures.

17. Why are the heats of formation of gaseous atoms from their elements endothermic quantities?
Solution
It is easy to see why the conversion of a solid or liquid element to gaseous atoms is an endothermic process. In the case of elements that exist naturally as gases, most are polyatomic (the exception are the noble gases). To convert these elements to gaseous atoms will require an input of energy as bonds need to be broken.

18. Show that for an isothermal expansion of an ideal gas, (a) $\Delta V = 0$ and (b) $\Delta H = 0$.
Solution
(a) We know that for 1 mol of an ideal gas $C_V = \left(\frac{dU}{dT}\right)_V$, hence, $dU = C_V dT$.
For a finite change, $\Delta U = C_V \Delta T$.
For isothermal process, T is constant so that $\Delta T = 0$.
Hence, $\Delta U = 0$.
(b) We know that $\Delta H = \Delta U + \Delta (pV)$
Since for an ideal gas, $pV = RT$

$$\Delta H = \Delta U + \Delta (RT) = \Delta U + R\Delta T$$

But $\Delta U = 0$ (proved above) and $\Delta T = 0$ (for isothermal process). Hence, $\Delta H = 0$.

19. Many reactions that have large, negative values of $\Delta G°$ are not actually observed to happen at 25°C and 1 atm. Why?
Solution
Although a reaction may have a favorable ΔG, and therefore be a spontaneous reaction in the thermodynamic sense of the word, the rate of reaction may be too slow at normal temperatures to be observed.

20. What factors must you consider to determine the sign of ΔS for the reaction $2HI(g) \rightarrow H_2(g) + I_2(s)$?
Solution
For the reaction $2HI(g) \rightarrow H_2(g) + I_2(g)$, the factors needed to be consider in order to determine the sign of ΔS are
(a) *The number of moles of products versus reactants*: In this case, the number of moles are the same.
(b) *The state of the products versus reactants*: Both products and reactants are gases.
(c) *The complexity of the molecules*: HI is more complex than either H_2 or I_2.
Hence, ΔS is expected to be negative.

21. Predict the algebraic sign of the entropy change for the following reactions:
(a) $I_2(s) \rightarrow I_2(g)$
(b) $Br_2(g) + 3Cl_2(g) \rightarrow 2BrCl_3(g)$
(c) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
(d) $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$
Solution
(a) ΔS is positive since randomness in a gas is higher than that in a solid.
(b) ΔS is negative. There are fewer moles of gases among the products.
(c) ΔS is negative since gaseous material (which is highly random) is replaced by a solid (which is highly ordered).

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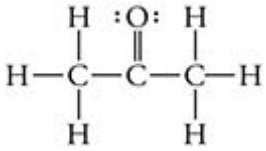
(d) ΔS is negative since the relatively random liquid reactant disappears in a process that makes only a solid.

22. Approximately how much energy would be released during the formation of the bonds in 1 mol of acetone molecules?



Solution
The energy released during the formation of 1 mol of acetone is equal to the sum of all of the bond energies in the molecule:
For the six C–H bonds: 412 kJ mol^{-1} × 6 mol C–H bonds
For the two C–C bonds: 348 kJ mol^{-1} × 2 mol C–C bonds
For the one C=O bond: 743 kJ mol^{-1} × 1 mol C=O bonds

Adding the above contributions, we get 3.91×10^3 kJ released per mole of acetone formed.

23. What is the value of the equilibrium constant for a reaction for which $\Delta G° = 0$? What will happen to the composition of the system if we begin the reaction with the pure products?
Solution

$$\Delta G^o = -2.303RT \log K$$

When $\Delta G° = 0$, K becomes

$$\log K = -\frac{\Delta G^o}{2.303RT} = 0 \Rightarrow K = 1$$

When $\Delta G° = 0$, the position of the equilibrium will lie midway between reactants and products. The reaction mixture at equilibrium will contain substantial amount of both reactants and products. The reaction will appear spontaneous whether we start from pure products or pure reactants. **24.** Which substance should have the more exothermic heat of formation, CF_4 or CCl_4?
Solution
The heat of formation of CF_4 should be more exothermic than that of CCl_4 because more energy is released on formation of a C–F bond than on formation of a C–Cl bond. Also, less energy is needed to form gaseous F atoms than to form gaseous Cl atoms.

25. (a) When an ideal gas expands at a constant temperature, $\Delta E = 0$ for the change. Why?
(b) When a real gas expands at a constant temperature, $\Delta E > 0$ for the change. Why?
Solution
(a) Under reversible conditions, the expansion of an ideal gas produces the maximum amount of work that can be obtained from the change. Such a situation cannot be accomplished by any real process. In an ideal gas, the gas particles are non-interacting. In a real gas, the interaction between the individual particles must be overcome so that the gas may expand. It requires an input of energy to overcome these attractive forces.

(b) The expansion of a real gas is not reversible, and not all of the free energy change for the process is converted to work as the gas expands. Some of the energy must be used to overcome the intermolecular forces of attraction that exist between molecules. In an ideal gas, the particles are assumed to be non-interacting and this energy loss is not a concern.

26. When potassium iodide dissolves in water, the mixture becomes cool. For this change, which is of

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a larger magnitude, $T\Delta S$ or ΔH?

Solution

First, review the information provided. Since the salt dissolved, the process is spontaneous, and the sign for ΔG is negative. The temperature went down indicating that this is an endothermic process and ΔH must be positive. Dissolving the solid salt increases the disorder of the system, which indicates ΔS is positive. The general equation from which we must work is $\Delta G = \Delta H - T\Delta S$. Using this equation, the magnitude of $T\Delta S$ must be larger than the magnitude of ΔH in order to obtain a negative value for ΔG. However, the magnitude of ΔH is almost certainly larger than that of ΔS as can be appreciated from the fact that ΔS° values are given in joules and those of ΔH_f^o are given in kilojoules.

27. The enthalpy of combustion, $\Delta_c H^\circ$ of oxalic acid, $H_2C_2O_4(s)$, is -246.05 kJ mol^{-1}. Consider the following data:

Substance	ΔH_f^o **(kJ mol^{-1})**	S° **(J mol^{-1} K^{-1})**
C(s)	0	5.69
$CO_2(g)$	–393.5	213.6
$H_2(g)$	0	130.6
$H_2O(l)$	–285.8	69.96
$O_2(g)$	0	205.0
$H_2C_2O_4(s)$	?	120.1

(a) Write the balanced thermochemical equation that describes the combustion of 1 mol of oxalic acid.

(b) Write the balanced thermochemical equation that describes the formation of 1 mol of oxalic acid.

(c) Use the information in the table above and the equations in parts (a) and (b) to calculate ΔH_f^o for oxalic acid.

(d) Calculate ΔS_f^o for oxalic acid and ΔS° for the combustion of 1 mol of oxalic acid.

(e) Calculate ΔG_f^o for oxalic acid and ΔG° for the combustion of 1 mol of oxalic acid.

Solution

(a) $H_2C_2O_4(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) + 2CO_2(g)$ $\quad \Delta H^\circ_{comb} = -246.05$ kJ

(b) $H_2(g) + 2C(s) + 2O_2(g) \rightarrow H_2C_2O_4(s)$ $\quad \Delta H_f^\circ = ?$ kJ mol^{-1}

(c) $\Delta H^\circ_{comb} = \{\Delta H_f^\circ(H_2O(l)) + 2\Delta H_f^\circ(CO_2(g))\} - \{\Delta H_f^\circ(H_2C_2O_4(s)) + \frac{1}{2}\Delta H_f^\circ(O_2(g))\}$

Rearranging, we get:

$\Delta H_f^\circ(H_2C_2O_4(s)) = \{\Delta H_f^\circ(H_2O(l)) + 2\Delta H_f^\circ(CO_2(g))\}$

$-\Delta H^\circ_{comb} = -285.8$ kJ $+ 2(-393.5$ kJ$) - (-246.05$ kJ$) = -826.8$ kJ

(d) $\Delta S_f^\circ = S^\circ(H_2C_2O_4(s)) - \{S_f^\circ(H_2(g)) + 2S^\circ(C(g)) + 2S^\circ(O_2(g))\}$

$= 120.1$ J K^{-1} $- \{130.6$ J K^{-1} $+ 2(5.69$ J K^{-1}$) + 2(205.0$ J K^{-1}$)\}$

$= -431.9$ J mol^{-1} K^{-1}

$\Delta S^\circ_{comb} = \{S^\circ(H_2O(l)) + 2S^\circ(CO_2(g))\} - \{S^\circ(H_2C_2O_4(g)) + (1/2)S^\circ(O_2(g))\}$

$= \{69.96$ J K^{-1} $+ 2(213.6$ J K^{-1}$)\} - \{120.1$ J K^{-1} $+ (1/2)(205.0$ J K^{-1}$)$

$= 274.6$ J mol^{-1} K^{-1}

(e) $\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ$

$= -826.8$ kJ $- (298$ K$)(-0.4319$ kJ K^{-1}$) = -698.1$ kJ

$\Delta G^\circ_{comb} = \Delta H^\circ_{comb} - T\Delta S^\circ_{comb}$

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$= -246.05 \text{ kJ} - (298 \text{ K})(0.2746 \text{ kJ K}^{-1}) = -327.9 \text{ kJ}$

Numerical Problems

1. A 5.00 g mass of a metal was heated to 100.0°C and then plunged into 100.0 g of water at 24.0°C. The temperature of the resulting mixture became 28.0°C.

(a) How many joules did the water absorb?
(b) How many joules did the metal lose?
(c) What is the heat capacity of the metal sample?
(d) What is the specific heat of the metal?

Solution

(a) $J = 4.184 \text{ J g}^{-1} \text{°C}^{-1} \times 100 \text{ g} \times 4.0\text{°C} = 1.67 \times 10^3 \text{ J}$

(b) $1.67 \times 10^3 \text{ J}$

(c) $\dfrac{1.67 \times 10^3 \text{ J}}{(100 - 28.0)\text{°C}} = 23.2 \text{ J°C}^{-1}$

(d) $\dfrac{23.2 \text{ J°C}^{-1}}{5.00 \text{ g}} = 4.64 \text{ J g}^{-1} \text{°C}^{-1}$

2. A sample of copper was heated to 120.00°C and then thrust into 200.0 g of water at 25.00°C. The temperature of the mixture became 26.50°C.

(a) How much heat in joules was absorbed by the water?
(b) The copper sample lost how many joules?
(c) What was the mass in grams of the copper sample?

Solution

(a) $J = 4.184 \text{ J g}^{-1} \text{°C}^{-1} \times 200.0 \text{ g} \times 1.50\text{°C} = 1.255 \times 10^3 \text{ J}$

(b) $1.255 \times 10^3 \text{ J}$

(c) $1.26 \times 10^3 \text{ J} = 0.387 \text{ J g}^{-1} \text{°C}^{-1} \times (120\text{°C} - 26.50\text{°C}) \times X \text{ g}$

$X = 34.7 \text{ g}$

3. What is the molar heat capacity of ethyl alcohol, C_2H_5OH, in units of J mol^{-1} °C^{-1}, if its specific heat is 0.586 cal g^{-1} °C^{-1}?

Solution

$$\frac{\text{J}}{\text{mol °C}} = \left(\frac{0.586 \text{ cal}}{\text{g °C}}\right)\left(\frac{4.184 \text{ J}}{\text{cal}}\right)\left(\frac{46.08 \text{ g } C_2H_5OH}{1 \text{ mol } C_2H_5OH}\right) = 113 \text{ J mol}^{-1} \text{°C}^{-1}$$

4. A dilute solution of hydrochloric acid with a mass of 610.29 g and containing 0.33183 mol of HCl was exactly neutralized in a calorimeter by the sodium hydroxide in 615.31 g of a dilute NaOH solution. The temperature increased from 16.784 to 20.610°C. The specific heat of the HCl solution was 4.031 J g^{-1} °C^{-1}; that of the NaOH solution was 4.046 J g^{-1} °C^{-1}. The heat capacity of the calorimeter was 77.99 J °C^{-1}. Write the balanced equation for the reaction. Use the data above to calculate the heat evolved. What is the heat of neutralization per mole of HCl? Assume that the original solutions made independent contributions to the total heat capacity of the system following their mixing.

Solution

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

The heat of neutralization is released to three "independent" components of the system, all of which undergo the same temperature increase: $\Delta T = 20.610\text{°C} - 16.784\text{°C} = 3.826\text{°C}$. Also, the total heat capacity of the system is the sum of the three heat capacities:

Heat capacity$_{HCl}$ + Heat capacity$_{NaOH}$ + Heat capacity$_{calorimeter}$

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$= (4.031\ J\ g^{-1}\ °C^{-1} \times 610.29\ g) + (4.046\ J\ g^{-1}\ °C^{-1} \times 615.31\ g) + 77.99\ J\ °C^{-1}$
$= 5028\ J\ °C^{-1}$

The heat flow to the system is thus:

$$\text{Heat} = 5028\ J\ °C^{-1} \times 3.826\ °C = 1.924 \times 10^4\ J = 19.24\ kJ$$

and the heat of neutralization is the negative of this value, since the neutralization process is exothermic:

$$\Delta H = \frac{-19.24\ kJ}{0.33183\ mol} = -57.98\ kJ\ mol^{-1}$$

5. A 1.500 g sample of liquid toluene was placed in a bomb calorimeter along with excess oxygen. When the combustion of the toluene was initiated, the temperature of the calorimeter rose from 25.000°C to 26.413°C. The products of the combustion are $CO_2(g)$ and $H_2O(l)$, and the heat capacity of the calorimeter was 45.06 kJ °C^{-1}.

(a) Write the balanced chemical equation for the reaction in the calorimeter.
(b) How many joules were liberated by the reaction?
(c) How many joules would be liberated under similar conditions if 1.00 mol of toluene were burned?

Solution

(a) $C_7H_8(l) + 9O_2(g) \rightarrow 7CO_2(g) + 4H_2O(l)$

(b) $J = (45.06\ kJ\ °C^{-1})(26.413°C - 25.000°C) = 63.67\ kJ = 6.367 \times 10^4\ J$

(c) $J = (1\ mol\ C_7H_8)\left(\frac{6.367 \times 10^4\ J}{1.500\ g}\right)\left(\frac{92.14\ g\ C_7H_8}{1\ mol\ C_7H_8}\right) = 3.911 \times 10^6\ J$

6. Ammonia reacts with oxygen as follows.

(a) Calculate the enthalpy change for the combustion of 1 mol of NH_3.
(b) Write the thermochemical equation for the reaction in which 1 mol of H_2O is formed.

$$4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(g) \quad \Delta H° = -1132\ kJ$$

Solution

(a) Divide the given equation by 4.

$$NH_3(g) + \tfrac{7}{4}O_2(g) \rightarrow NO_2(g) + \tfrac{3}{2}H_2O(g)\ \Delta H° = -1132\ kJ/4 = -283\ kJ$$

(b) Divide the given equation by 6

$$\tfrac{2}{3}NH_3(g) + \tfrac{7}{6}O_2(g) \rightarrow \tfrac{2}{3}NO_2(g) + H_2O(g)\ \Delta H° = -1132\ kJ/6 = -189\ kJ$$

7. Construct an enthalpy diagram for the formation of $NO_2(g)$ from its elements by two pathways: first, from its elements and, second, by a two-step process, also from the elements. The relevant thermochemical equations are

$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta H° = +33.8\ kJ$

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g) \qquad \Delta H° = +90.37\ kJ$

$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g) \qquad \Delta H° = ?$

Be sure to note the signs of the values of $\Delta H°$ associated with arrows pointing up or down. Using the diagram, determine the value of $\Delta H°$ for the third equation.

Solution

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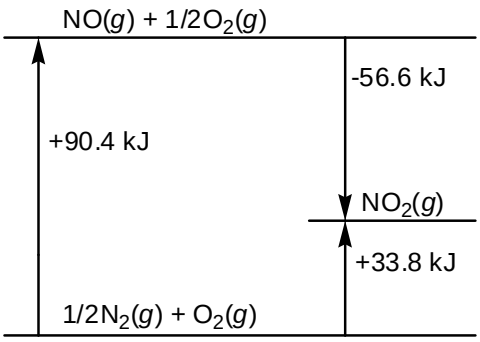

8. A 2kg piece of granite with a specific heat of 0.803 J g^{-1} C^{-1} and a temperature of 95°C is placed into 2 L of water at 22.0°C. When the granite and water come to the same temperature, what will that temperature be?

Solution

Heat lost = (2000 g)(0.803 J g^{-1} °C^{-1})(95°C – x°C)

= (1606 J °C^{-1})(95°C – x°C)

=152,600 J – (1606 J)(x°C)

Heat gained = (2.00 L) $\left(\frac{1000\text{ mL}}{1\text{ L}}\right)\left(\frac{1\text{ g}}{1\text{ mL}}\right)\left(\frac{4.184\text{ J}}{\text{g }^\circ\text{C}}\right)\left(x - 22^\circ\text{C}\right)$

= (8368 J °C^{-1})(x°C – 22°C)

= (8368 J)(x°C) – 184,100 J

where x = Final temperature; we can solve for x since Heat lost = Heat gained.

152,600 J – (1606 J)(x°C) = (8368 J)(x°C) – 184,100 J

336,700 J = (9974 J)(x°C) ⇒ x = 33.8°C

9. Suppose a truck with a mass of 14 tons (1 ton = 907.18 kg) is traveling at a speed of 72.42 km h^{-1}. If the truck driver slams on the brakes, the kinetic energy of the truck is changed to heat as the brakes slow the truck to a stop. How much would the temperature of 19 L of water increase if all the heat could be absorbed by the water?

Solution

Kinetic Energy = $\frac{1}{2}mv^2 = \frac{1}{2}$ (14.0 tons)

$$\times \left(\frac{2000\text{ lb}}{1\text{ ton}}\right)\left(\frac{453.6\text{ g}}{1\text{ lb}}\right)\left(\frac{1\text{ kg}}{1000\text{ g}}\right)\left[\left(\frac{45.0\text{ mi}}{\text{hr}}\right)\left(\frac{1\text{ hr}}{3600\text{ s}}\right)\left(\frac{5280\text{ ft}}{1\text{ mi}}\right)\left(\frac{30.48\text{ cm}}{1\text{ ft}}\right)\left(\frac{1\text{ m}}{100\text{ cm}}\right)\right]^2$$

= 2.57×10^6 J = 2.57×10^3 kJ

Water (in grams) = (5.00 gal) $\left(\frac{3.785\text{ L}}{1\text{ gal}}\right)\left(\frac{1000\text{ mL}}{1\text{ L}}\right)\left(\frac{1\text{ g}}{1\text{ mL}}\right)$ = 18900 g water

Increasing the temperature of water:

2.57×10^6 J = (4.184 J g^{-1} °C^{-1})(18900 g)(ΔT) ⇒ ΔT = 32°C

10. Ethanol, C_2H_5OH, is made industrially by the reaction of water with ethylene, C_2H_4. Calculate the value of ΔH° for the reaction

$C_2H_4(g) + H_2O(l) \rightarrow C_2H_5OH(l)$

Given the following thermochemical equations,

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$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l); \quad \Delta H^\circ = -1411.1 \text{ kJ}$$
$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l); \quad \Delta H^\circ = -1367.1 \text{ kJ}$$

Solution

This problem requires that we add the reverse of the second equation (remembering to change the sign of the associated ΔH value) to the first equation:

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l); \ \Delta H° = -1411.1 \text{ kJ mol}^{-1}$$
$$2CO_2(g) + 3H_2O(l) \rightarrow C_2H_5OH(l) + 3O_2(g); \ \Delta H° = +1367.1 \text{ kJ kJ mol}^{-1}$$

which gives the following net equation and value for $\Delta H°$:

$$C_2H_4(g) + H_2O(l) \rightarrow C_2H_5OH(l); \ \Delta H° = -44.0 \text{ kJ mol}^{-1}$$

11. Calculate the maximum work that could be obtained from the combustion of 100 g of ethanol, $C_2H_5OH(l)$. How does it compare with the maximum work from the combustion of 100 g of $C_8H_{18}(l)$? Which is the better fuel? (*Hint*: The work available *per mole* has already been calculated in the worked examples.)

Solution

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

$$\Delta G^\circ_{rxn} = \{2\,\Delta G^\circ_f[CO_2(g)] + 3\,\Delta G^\circ_f[H_2O(l)]\} - \{\Delta G^\circ_f[C_2H_5OH(l)] + 3\,\Delta G^\circ_f[O_2(g)]\}$$
$$= \{2 \text{ mol} \times (-394.4 \text{ kJ mol}^{-1}) + 3 \text{ mol} \times (-237.2 \text{ kJ mol}^{-1})\} - \{1 \text{ mol} \times (-174.8 \text{ kJ mol}^{-1}) + 3 \text{ mol} \times (0 \text{ kJ mol}^{-1})\}$$
$$= -1325.6 \text{ kJ}$$

For 100 g C_2H_5OH:

$$\text{mol } C_2H_5OH = 100 \text{ g } C_2H_5OH \left(\frac{1 \text{ mol } C_2H_5OH}{46.08 \text{ g } C_2H_5OH}\right) = 2.17 \text{ mol } C_2H_5OH$$

Maximum work:

$$(1325.6 \text{ kJ mol}^{-1})(2.17 \text{ mol } C_2H_5OH) = 2877 \text{ kJ}$$

$C_8H_{18}(l) + \frac{25}{2} O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$

$$\Delta G^\circ_{rxn} = \{8\,\Delta G^\circ_f[CO_2(g)] + 9\,\Delta G^\circ_f[H_2O(l)]\} - \{\Delta G^\circ_f[C_8H_{18}(l)] + \frac{25}{2}\,\Delta G^\circ_f[O_2(g)]\}$$
$$= \{8 \text{ mol} \times (-394.4 \text{ kJ mol}^{-1}) + 9 \text{ mol} \times (-237.2 \text{ kJ mol}^{-1})\} - \{1 \text{ mol} \times (+17.3 \text{ kJ mol}^{-1}) + \frac{25}{2} \text{ mol} \times (0 \text{ kJ mol}^{-1})\}$$
$$= -5304.1 \text{ kJ}$$

For 100 g C_8H_{18}:

$$\text{mol } C_8H_{18} = 100 \text{ g } C_8H_{18} \left(\frac{1 \text{ mol } C_8H_{18}}{114.26 \text{ g } C_8H_{18}}\right) = 0.875 \text{ mol } C_8H_{18}$$

Maximum work:

$$(5304.1 \text{ kJ mol}^{-1})(0.875 \text{ mol } C_8H_{18}) = 4640 \text{ kJ}$$

The octane is a better fuel on both a per gram and per mole basis.

12. The heat of vaporization of mercury is 60.7 kJ mol^{-1}. For Hg(l), $S°$ = 76.1 J mol^{-1} K^{-1} and for Hg(g), $S°$ = 175 J mol^{-1} K^{-1}. Estimate the normal boiling point of liquid mercury.

Solution

For the vaporization process in particular, and for any process in general, we have:

$$\Delta G = \Delta H - T\Delta S$$

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If the temperature is taken to be that at which equilibrium is obtained, that is, the temperature of the boiling point (where liquid and vapor are in equilibrium with one another), then we also have the result that ΔG is equal to zero:

$$\Delta G = 0 = \Delta H - T\Delta S, \text{ or } T_{eq} = \Delta H/\Delta S$$

We know ΔH to be 60.7 kJ mol^{-1}; we need the value for ΔS in units kJ mol^{-1} K^{-1}:

$$\begin{aligned}\Delta S° &= (\text{sum } S°[\text{Products}]) - (\text{sum } S°[\text{Reactants}])\\ &= S°[\text{Hg(g)}] - S°[\text{Hg(l)}]\\ &= (175 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}) - (76.1 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})\\ &= 98.9 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}\end{aligned}$$

So, the normal boiling point of liquid mercury is

$$T_{eq} = 60.7 \text{ kJ mol}^{-1} \div 98.9 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K} = 614 \text{ K } (341°\text{C})$$

13. Suppose that you were pumping an automobile tire with a hand pump that pushed 24.0 in^3 of air into the tire on each stroke, and that during one such stroke the opposing pressure in the tire was 30.0 lb in^{-2} above the normal atmospheric pressure of 14.7 lb in^{-2}. Calculate the number of joules of work accomplished during each stroke. (1 L atm = 101.325 J.)

Solution

We know that Work = $p \times \Delta V$. The total pressure is atmospheric pressure plus that caused by the hand pump:

$$p = (30.0 + 14.7) \text{ lb in}^{-2} = 44.7 \text{ lb in}^{-2}$$

Converting to atmospheres we get:

$$p = 44.7 \text{ lb in}^{-2} \times 1 \text{ atm}/14.7 \text{ lb in}^{-2} = 3.04 \text{ atm}$$

Next we convert the volume change in units in^3 to units L:

$$24.0 \text{ in}^3 \times (2.54 \text{ cm in}^{-1})^3 \times 1 \text{ L}/1000 \text{ cm}^3 = 0.393 \text{ L}$$

Hence, $p \times \Delta V = (3.04 \text{ atm})(0.393 \text{ L}) = 1.19 \text{ L·atm}$

$$1.19 \text{ L·atm} \times 101.3 \text{ J L}^{-1}\text{·atm}^{-1} = 121 \text{ J}$$

14. A 10 L vessel at 20°C contains butane, C_4H_{10}(g), at a pressure of 2.00 atm. What is the maximum amount of work that can be obtained by the combustion of this butane if the gas is first brought to a pressure of 1 atm and the temperature is brought to 25°C? Assume the products are also returned to that same temperature and pressure.

Solution

$$C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$$

Find the moles of C_4H_{10} at the first set of pressure, volume, and temperature data, then find the moles of the CO_2 and H_2O resulting from the reaction. Finally, find the new volume of the products.

$pV = nRT$

$$\text{mol } C_4H_{10} = \frac{(2.00 \text{ atm})(10.0 \text{ L})}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(293 \text{ K})} = 0.831 \text{ mol } C_4H_{10}$$

$$\text{mol } CO_2 = (0.831 \text{ mol } C_4H_{10})\left(\frac{4 \text{ mol } CO_2}{1 \text{ mol } C_4H_{10}}\right) = 3.32 \text{ mol } CO_2$$

$$\text{mol } H_2O = (0.831 \text{ mol } C_4H_{10})\left(\frac{5 \text{ mol } H_2O}{1 \text{ mol } C_4H_{10}}\right) = 4.16 \text{ mol } H_2O$$

Total moles of product = 3.32 mol CO_2 + 4.16 mol H_2O = 7.48 mol

$$\text{Initial volume} = \frac{(0.831 \text{ mol})(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{1.00 \text{ atm}} = 20.3 \text{ L}$$

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Final volume = $\dfrac{(7.48\text{ mol})(0.0821\text{ L atm mol}^{-1}\text{ K}^{-1})(298\text{ K})}{1.00\text{ atm}}$ = 183 L

$w = -p\Delta V = -$ (1.00 atm)(183 L – 20.3 L) = 163 L atm

In kilojoules: 163 L atm $\left(\dfrac{101.325\text{ J}}{1\text{ L atm}}\right)\left(\dfrac{1\text{ kJ}}{1000\text{ J}}\right)$ = 16.5 kJ

15. Calculate the entropy change when 1.8 g of water is completely converted into vapor at 100°C. The molar heat of vaporization is 40.85 kJ mol^{-1}.

Solution

$\Delta S°$ = (sum $S°$[Products]) – (sum $S°$[Reactants])

= {$2S°[HNO_3(l)] + S°[NO(g)]$} – {$3S°[NO_2(g)] + S°[H_2O(l)]$}

= {2 mol × (155.6 J mol^{-1} K^{-1}) + 1 mol × (210.6 J mol^{-1} K^{-1})}

– {3 mol × (240.5 J mol^{-1} K^{-1}) + 1 mol × (69.96 J mol^{-1} K^{-1})}

= –269.7 J K^{-1}

16. Alcohol is oxidized to acetic acid if it is exposed to air. The equation for the reaction is

$$C_2H_5OH(l) + O_2(g) \rightarrow CH_3COOH\ (l) + H_2O(l)$$

Calculate $\Delta S°$ for the reaction in J K^{-1}.

Solution

$\Delta S°$ = (sum $S°$[Products]) – (sum $S°$[Reactants])

= {$S°[HC_2H_3O_2(l)] + S°[H_2O(l)]$} – {$S°[C_2H_5OH(l)] + S°[O_2(g)]$}

= {1 mol × (160 J mol^{-1} K^{-1}) + 1 mol × (69.96 J mol^{-1} K^{-1})}

– {1 mol × (161 J mol^{-1} K^{-1}) + 1 mol × (205.0 J mol^{-1} K^{-1})}

= –136 J K^{-1}

17. Phosgene, $COCl_2$, was used as a war gas during World War I. It reacts with the moisture in the lungs to produce HCl, which causes the lungs to fill with fluid, and CO, which asphyxiates the victim. Both lead ultimately to death. For $COCl_2$(g), $\Delta S°$ = 284 J mol^{-1} K^{-1} and ΔH_f^o = –223 kJ mol^{-1}. Use this information and the data in Table 6.3 to calculate ΔG_f^o for $COCl_2$(g) in kJ mol^{-1}.

Solution

The quantity ΔG_f° applies to the equation in which 1 mol of pure phosgene is produced from the naturally occurring forms of the elements:

$$C(s) + \tfrac{1}{2}O_2(g) + Cl_2(g) \rightarrow COCl_2(g),\ \Delta G_f^\circ = ?$$

We can determine ΔG_f° if we can find values for ΔH_f° and ΔS_f°, because:

$$\Delta G° = \Delta H° - T\Delta S°$$

The value of ΔS_f° is determined using $S°$ for phosgene in the following way:

ΔS_f° = {$S°[COCl_2(g)]$} – {$S°[C(s)] + \frac{1}{2}S°[O_2(g)] + S°[Cl_2(g)]$}

= {1 mol × (284 J mol^{-1} K^{-1})} – {1 mol × (5.69 J mol^{-1} K^{-1})

+ $\frac{1}{2}$ mol × (205.0 J mol^{-1} K^{-1}) + 1 mol × (223.0 J mol^{-1} K^{-1})}

= –47 J mol^{-1} K^{-1} or –47 J/K

$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ$ = –223 kJ mol^{-1} – (298 K)(–0.047 kJ mol^{-1} K^{-1})

= –209 kJ mol^{-1}

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18. Gasohol is a mixture of gasoline and ethanol (grain alcohol), C_2H_5OH. Calculate the maximum work that could be obtained at 25°C and 1 atm by burning 1 mol of C_2H_5OH.

Solution

The maximum work obtainable from a reaction is equal in magnitude to the value of ΔG for the reaction. Thus, we need only determine $\Delta G°$ for the process:

$$\Delta G° = (\text{sum } \Delta G_f^\circ\,[\text{Products}]) - (\text{sum } \Delta G_f^\circ\,[\text{Reactants}])$$
$$= \{3\,\Delta G_f^\circ\,[H_2O(g)] + 2\,\Delta G_f^\circ\,[CO_2(g)]\} - \{3\,\Delta G_f^\circ\,[O_2(g)] + \Delta G_f^\circ\,[C_2H_5OH(l)]\}$$
$$= \{3 \text{ mol} \times (-228.6 \text{ kJ mol}^{-1}) + 2 \text{ mol} \times (-394.4 \text{ kJ mol}^{-1})\}$$
$$- \{3 \text{ mol} \times (0.0 \text{ kJ mol}^{-1}) + 1 \text{ mol} \times (-174.8 \text{ kJ mol}^{-1})\}$$
$$= -1299.8 \text{ kJ}$$

19. For the melting of aluminum, $Al(s) \rightarrow Al(l)$, $\Delta H° = 10.0$ kJ mol^{-1} and $\Delta S° = 9.50$ J mol^{-1} K^{-1}. Calculate the melting point of Al. (The actual melting point is 660°C.)

Solution

At equilibrium, $\Delta G = 0 = \Delta H - T\Delta S$

$T_{eq} = \Delta H/\Delta S$, and assuming that ΔS and ΔH are independent of temperature, we have:

$= (10.0 \times 10^3 \text{ J mol}^{-1}) \div (9.50 \text{ J mol}^{-1} \text{ K}^{-1}) = 1.05 \times 10^3$ K or 780°C

Apparently, ΔH and ΔS are not independent of temperature!

20. Which of the following reactions (equations unbalanced) would be expected to be spontaneous at 25°C and 1 atm?

(a) $PbO(s) + NH_3(g) \rightarrow Pb(s) + N_2(g) + H_2O(g)$

(b) $NaOH(s) + HCl(g) \rightarrow NaCl(s) + H_2O(l)$

(c) $Al_2O_3(s) + Fe(s) \rightarrow Fe_2O_3(s) + Al(s)$

(d) $2CH_4(g) \rightarrow C_2H_6(g) + H_2(g)$

Solution

We first balance each equation, and then calculate a value of $\Delta G°$. If $\Delta G°$ is a negative number, then the reaction is spontaneous.

(a) $3PbO(s) + 2NH_3(g) \rightarrow 3Pb(s) + N_2(g) + 3H_2O(g)$

$$\Delta G° = \{3\,\Delta G_f^\circ\,[Pb(s)] + \Delta G_f^\circ\,[N_2(g)] + 3\,\Delta G_f^\circ\,[H_2O(g)]\}$$
$$- \{3\,\Delta G_f^\circ\,[PbO(s)] + 2\,\Delta G_f^\circ\,[NH_3(g)]\}$$
$$= \{3 \text{ mol} \times (0.0 \text{ kJ mol}^{-1}) + 1 \text{ mol} \times (0.0 \text{ kJ mol}^{-1})$$
$$+ 3 \text{ mol} \times (-228.6 \text{ kJ mol}^{-1})\} - \{3 \text{ mol} \times (-189.3 \text{ kJ mol}^{-1}) + 2 \text{ mol} \times (-16.7 \text{ kJ mol}^{-1})\}$$
$$= -84.5 \text{ kJ}$$

So, the reaction is spontaneous.

(b) $NaOH(s) + HCl(g) \rightarrow NaCl(s) + H_2O(l)$

$$\Delta G° = \{\Delta G_f^\circ\,[NaCl(s)] + \Delta G_f^\circ\,[H_2O(l)]\} - \{\Delta G_f^\circ\,[NaOH(s)] + \Delta G_f^\circ\,[HCl(g)]\}$$
$$= \{1 \text{ mol} \times (-384.0 \text{ kJ mol}^{-1}) + 1 \text{ mol} \times (-237.2 \text{ kJ mol}^{-1})\}$$
$$- \{1 \text{ mol} \times (-382 \text{ kJ mol}^{-1}) + 1 \text{ mol} \times (-95.27)\}$$
$$= -144 \text{ kJ}$$

So, the reaction is spontaneous.

(c) $Al_2O_3(s) + 2Fe(s) \rightarrow Fe_2O_3(s) + 2Al(s)$

$$\Delta G° = \{\Delta G_f^\circ\,[Fe_2O_3(s)] + 2\,\Delta G_f^\circ\,[Al(s)]\} - \{\Delta G_f^\circ\,[Al_2O_3(s)] + 2\,\Delta G_f^\circ\,[Fe(s)]\}$$
$$= \{1 \text{ mol} \times (-741.0 \text{ kJ mol}^{-1}) + 2 \text{ mol} \times (0.0 \text{ kJ mol}^{-1})\}$$

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$- \{1 \text{ mol} \times (-1576.4 \text{ kJ mol}^{-1}) + 2 \text{ mol} \times (0.0 \text{ kJ mol}^{-1})\}$

$= +835.4$ kJ

So, the reaction is not spontaneous.

(d) $2CH_4(g) \rightarrow C_2H_6(g) + H_2(g)$

$\Delta G° = \{ \Delta G_f^\circ [C_2H_6(g)] + \Delta G_f^\circ [H_2(g)]\} - \{2 \Delta G_f^\circ [CH_4(g)]\}$

$= \{1 \text{ mol} \times (-32.9 \text{ kJ mol}^{-1}) + 1 \text{ mol} \times (0.0 \text{ kJ mol}^{-1})\}$

$- \{2 \text{ mol} \times (-50.79 \text{ kJ mol}^{-1})\}$

$= +68.7$ kJ

So, the reaction is not spontaneous.

21. The reaction $CO(g) + H_2O(g) \rightarrow HCHO_2(g)$ has $\Delta G^\circ_{673K} = +79.8$ kJ mol^{-1}. If a mixture at 400°C contains 0.040 mol CO, 0.022 mol H_2O, and 3.8×10^{-3} mol $HCHO_2$ in a 2.50 L container, is the reaction at equilibrium? If not, in which direction will the reaction proceed spontaneously?

Solution

$79.8 \times 10^3 \text{ J} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(673 \text{ K}) \times \ln K_p$

$\ln K_p = -14.3 \quad \therefore K_p = 6.40 \times 10^{-7}$

We start by calculating the reaction quotient, Q. Be sure to determine the pressure of the gases using the ideal gas law.

$$Q = \frac{\left(\dfrac{(3.8 \times 10^{-3} \text{ mol})(0.0821 \frac{\text{L atm}}{\text{mol K}})(673 \text{ K})}{2.50 \text{ L}}\right)}{\left(\dfrac{(0.040 \text{ mol})(0.0821 \frac{\text{L atm}}{\text{mol K}})(673 \text{ K})}{2.50 \text{ L}}\right)\left(\dfrac{(0.022 \text{ mol})(0.0821 \frac{\text{L atm}}{\text{mol K}})(673 \text{ K})}{2.50 \text{ L}}\right)} = 0.195$$

Since the value of Q is larger than the value of K_p, the system must shift to the left in order to reach equilibrium.

22. The standard heat of formation of ethylene, $C_2H_4(g)$, is +52.284 kJ mol^{-1}. Calculate the C=C bond energy in this molecule. The C–H bond energy is 412 kJ·mol^{-1}.

Solution

The bond energy reaction is $2C(g) + 4 H(g) \rightarrow C_2H_4(g)$.

For determining the heat of formation, we need to reverse the reaction as follows:

$C_2H_4(g) \rightarrow 2C(s) + 2 H_2(g)$, $\Delta H° = -52.284$ kJ mol^{-1}

Now, for the p

$2C(s) \rightarrow 2C(g)$, $\Delta_r H^\circ = 2(716.67) = 1433.34$ kJ mol^{-1}

For the atomization reaction

$2 H_2 (g) \rightarrow 4 H(g)$, $\Delta_r H^\circ = 4(217.89) = 871.56$ kJ mol^{-1}

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Thus, for the formation reaction in gaseous phase, the heat of reaction is

$C_2H_4(g) \rightarrow 2C(g) + 4\ H(g)$,

$$\Delta H^o = -52.284 + 1433.34 + 871.56 = +2252.6 \text{ kJ mol}^{-1}$$

Relating heat of reaction of formation with bond energies, we have:

[4(C–H) + C=C] = 4(412) + [C=C] = (+2252.6 kJ)

1648 kJ + [C=C] = (+2252.6 kJ)

Solving, we get [C=C] = 2252.6 – 1648 = 605 kJ

23. If pressure is expressed in atmospheres and volume is expressed in liters, $p\Delta V$ has units of L atm (liters × atmospheres). Using 1 atm = 101,325 Pa, and 1 L = 1 dm^3, determine the number of joules corresponding to 1 L atm.

Solution

p(atm) × ΔV(L) = 1 L atm of work

Substituting the given information, we get

$$p \times \Delta V = 101{,}325 \text{ Pa} \times 1 \text{ dm}^3$$

Now it is true that 1 dm = 0.1 m, so,

$$1 \text{ dm}^3 = (0.1 \text{ m})^3 = 1 \times 10^{-3} \text{ m}^3$$

Also, 1 Pa = 1 N m^{-2}. Thus we have:

$$p(\text{Pa}) \times \Delta V(\text{dm}^3) = (101{,}325 \text{ N m}^{-2})(1 \times 10^{-3} \text{ m}^3) = 101.325 \text{ N·m}$$

$$101.325 \text{ N·m} \times 1 \text{ J}/1 \text{ N·m} = 101.325 \text{ J}$$

or

$$1 \text{ L atm} \times \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{0.021 \text{ L atm mol}^{-1} \text{ K}^{-1}} = 101.325 \text{ J}$$

24. Use the data in Table 6.3 to calculate the bond energy in the nitrogen molecule and the oxygen molecule.

Solution

The reaction is $N_2(g) \rightarrow 2N(g)$, $\Delta H° = 2\,\Delta H_f^\circ[N(g)] - \Delta H_f^\circ[N_2(g)]$. Since the enthalpy of formation of molecular nitrogen is defined as zero, the enthalpy change for this reaction and, consequently, the bond energy of a nitrogen molecule, is simply two times the enthalpy of formation of atomic nitrogen.

$$\text{Bond energy} = (2 \text{ mol N atoms})\left(\frac{472.68 \text{ kJ}}{\text{mol N atoms}}\right) = 945.36 \text{ kJ}$$

A similar argument holds true for oxygen:

$$\text{Bond energy} = (2 \text{ mol O atoms})\left(\frac{249.17 \text{ kJ}}{\text{mol N atoms}}\right) = 498.34 \text{ kJ}$$

Additional Objective Questions

Single Correct Choice Type

1. Among mass, volume, density and specific volume of a gas, the intensive properties are

(A) density and specific volume. (B) volume and density.

(C) specific volume and mass. (D) density only.

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Solution
(A) Density is mass per unit volume and specific volume is volume per unit mass.

2. Heats of combustion of CH_4, C_2H_4, and C_2H_6 are –890, –1411 and –1560 kJ mol^{-1}, respectively. Which has the lowest fuel value in kJ g^{-1}?
(A) CH_4 (B) C_2H_4 (C) C_2H_6 (D) All same
Solution
(B) The values given to us are in per mole, so for per gram, we divide by their respective molecular masses.

The heat of combustion of per gram of CH_4 $= -\frac{890}{16} = -55.625$ kJ

The heat of combustion of per gram of C_2H_4 $= -\frac{1411}{28} = -50.393$ kJ

The heat of combustion of per gram of C_2H_6 $= -\frac{1560}{30} = -52$ kJ

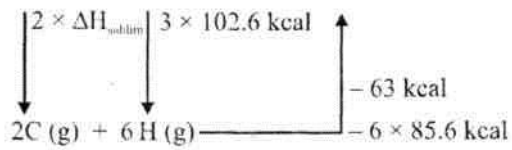
Hence, C_2H_4 is the lowest.

3. The heat of formation of HCl(g) from the reaction $H_2(g) + Cl_2(g) \rightarrow 2HCl$; $\Delta H = -44$ kcal is
(A) +44 kcal. (B) –44 kcal. (C) +22 kcal. (D) –22 kcal.
Solution
(D) The heat of formation of HCl is to be calculated on per mole of HCl produced

Heat of formation of HCl = $\frac{44}{2} = -22$ kcal. (as $\Delta H = -44$ kcal per 2 mol of HCl)

4. The bond energies of C–C and C–C at 298 K are 590 and 331 kJ mol^{-1}, respectively. The enthalpy of polymerization per mole of ethylene is
(A) –70 kJ. (B) –72 kJ. (C) 72 kJ. (D) –68 kJ.
Solution
(B) Polymerization reaction $n\,CH_2 = CH_2 \rightarrow (CH_2 - CH_2)_n$
1 mol of C = C bond is broken and 2 mol of C – C bonds are formed per mole of ethylene.
$\Delta H = 590 - 2 \times 331 = 590 - 662$ 590 is spent, and 2×331 is formed.
$= -72$ kJ mol^{-1} of ethylene.

5. ΔH for the reaction $2C(s) + 3H_2(g) \rightarrow C_2H_6(g)$ is –20.24 kcal mol^{-1}. To what value of the enthalpy of sublimation of C(s) does this point. Given that the bond energies of C–C, C–H and H–H are 63 kcal mol^{-1}, 85.6 kcal mol^{-1} and 102.6 kcal mol^{-1}.
(A) 124.3 kcal mol^{-1} (B) 185.3 kcal mol^{-1} (C) 158.3 kcal mol^{-1} (D) 211.5 kcal mol^{-1}
Solution
(A) $2C(s) + 3H_2(g) \rightarrow C_2H_6(g)$; $\Delta H = -20.24$ kcal mol^{-1}



$\Delta H_{sublimation}$ is the enthalpy (s → g)
$[2 \times \Delta H_{sublimation}] + 307.8 - 63 - 513.6 = -20.24$
$2 \times \Delta H_{sublimation} = [-20.24 + 63 + 513.6 - 307.8]$ kcal
$\Delta H_{sublimation} = 124.3$ kcal mol^{-1} of carbon.

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6. If the enthalpy change for the transition of liquid water to steam is 30 kJ mol^{-1} at 27°C, the entropy change for the process would be (in J mol^{-1} K^{-1})

(A) 100 (B) 10 (C) 1.0 (D) 0.1

Solution

(A) $H_2O(l) \rightarrow H_2O(g)$; ΔH = 30 kJ mol^{-1} where T = 300 K, therefore,

$$\Delta S = \frac{\Delta_{trans} H}{T} = \frac{30 \times 10^3}{300} = 100 \text{ J mol}^{-1}\text{K}^{-1}$$

7. Which of the following reactions represents $\Delta_{hyd}H$:

(A) $CuSO_4(s)\ (aq) \rightarrow CuSO_4(aq)$; $\Delta H = -x$ kJ

(B) $BaCl_2(s) + 2H_2O(l) \rightarrow BaCl_2 + 2H_2O(s)$; $\Delta H = -y$ kJ

(C) $CuSO_4(s) + 5H_2O(l)\ (aq) \rightarrow CuSO_4{\cdot}5H_2O(aq)$; $\Delta H = -z$ kJ

(D) None of these

Solution

(C) Enthalpy of hydration is the amount of enthalpy change when 1 mol of the anhydrous salt combines with the required number of moles of water so as to change into the hydrated salt.

8. Which one of the following statements is false?

(A) Work is a state function.

(B) Temperature is a state function.

(C) Work appears at the boundary of the system.

(D) Change in the state is completely defined when the initial and final states are specified.

Solution

(A) Work is not a state function; instead it is dependent on the path of the reaction.

9. A gas mixture consisting of 3.67 L of ethylene and methane on complete combustion at 25°C produces 6.11 L of CO_2. Find out the amount of heat evolved on burning 1 L of the gas mixture. The heats of combustion of ethylene and methane are –1423 and –891 kJ mol^{-1}, respectively, at 25°C

(A) 30.88 kJ (B) 20.28 kJ (C) 50.88 kJ (D) 60.18 kJ

Solution

(C) The combustion reactions are

$C_2H_4\ (g) + 3O_2\ (g) \rightarrow 2CO_2\ (g) + 2H_2O(l)$

$CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O(l)$

Let V be the volume of $C_2H_4(g)$ in the gaseous mixture of 3.67 L. From the chemical equations, we find that

Volume of $CO_2(g)$ produced due to the combustion of $C_2H_4(g) = 2V$

Volume of $CO_2(g)$ produced due to the combustion of $CH_4(g)$ = 3.67 L – V

Equating the latter with 6.11 L – 2 V, we get

$$3.67 \text{ L} - V = 6.11 \text{ L} - 2V \text{ or } V = 2.44 \text{ L}$$

Hence, in the original mixture, we have

Volume of $C_2H_4(g)$ per liter of the mixture $= \left(\frac{2.44 \text{ L}}{3.67 \text{ L}}\right)(1 \text{ L}) = 0.665 \text{ L}$

Volume of CH_4 (g) per liter of the mixture = 1.0 L – 0.665 L = 0.335 L

Now, volume of 1 mol of any gas at 25°C $= (22.414 \text{ L})\left(\frac{298 \text{ K}}{273 \text{ K}}\right) = 24.467 \text{ L}$

Hence, heat released due to the combustion of $CH_4(g) = (1423 \text{ kJ})\left(\frac{0.665 \text{ K}}{24.467 \text{ K}}\right) = 38.68 \text{ kJ}$

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Heat released due to the combustion of $CH_4(g) = (891\text{ kJ})\left(\frac{0.335\text{ K}}{24.467\text{ K}}\right) = 12.20\text{ kJ}$

Total heat released = (38.68 + 12.20) kJ = 50.88 kJ.

10. If 1 kcal of heat is added to 1.2 L of oxygen in a cylinder at constant pressure of 1 atm, the volume increases to 1.5 L. Hence, ΔU for this process is:

(A) 0.993 kcal (B) 1.0073 kcal (C) 0.0993 kcal (D) 1.00073 kcal

Solution

(A)

$\Delta H = \Delta E + p\Delta V$

$\Delta E = \Delta H - p\Delta V$

$\Delta E = 1\text{ kcal} - 1 \times 0.3\text{ L atm}$

$= 1\text{ kcal} - 0.3\text{ L atm} = 1\text{ kcal} - 0.3 \times 0.024\text{ kcal} = 1\text{ kcal} - 0.0072\text{ kcal} = 0.993\text{ kcal}$

11. For A $\rightarrow$ B, $\Delta H = 4$ kcal mol^{-1}, $\Delta S = 10$ cal mol^{-1} K^{-1}. Reaction is spontaneous when temperature can be

(A) 400 K (B) 300 K (C) 500 K (D) None of these.

Solution

(C) As $\Delta G = -$ve for spontaneous change and $\Delta G = \Delta H - T\Delta S$, we have

$$T\Delta S > \Delta H \Rightarrow T > \frac{\Delta H}{\Delta S} \Rightarrow T > \frac{4000}{10} \Rightarrow T > 400\text{ K}$$

12. If $\Delta G = \Delta H - T\Delta S$ and $\Delta G = \Delta H + T\left(\frac{d(\Delta G)}{dT}\right)_p$ then variation of EMF of a cell E, with temperature T is given by

(A) $\frac{\Delta H}{nF}$ (B) $\frac{\Delta G}{nF}$ (C) $\frac{\Delta S}{nF}$ (D) $-\frac{\Delta S}{nF}$

Solution

(C) On comparison: $\Delta S = \left[\frac{d(\Delta G)}{dt}\right] \Rightarrow \Delta S = \frac{d(-nFE)}{dT} = nF\left(\frac{dE}{dT}\right) \Rightarrow \left(\frac{dE}{dT}\right) = \frac{\Delta S}{nF}$

13. For the reaction X_2O_4 (l) $\rightarrow 2XO_2$(g), $\Delta U = 2.1$ kcal. $\Delta S = 20$ cal K^{-1} at 300 K. Then, ΔG is

(A) 2.7 kcal (B) –2.7 kcal (C) 9.3 kcal (D) –9.3 kcal

Solution

(B) $\Delta H = \Delta E + \Delta n_g RT = 2.1 + 2 \times 0.002 \times 300 = 3.03$ kcal; $\Delta n_g = 2 - 0 = 2$; $T = 300$ K

and $\Delta G = \Delta H - T\Delta S = 3.3 - 300 \times (0.02) = -2.7$ kcal

14. From the following data of ΔH, of the following reactions:

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$; ΔH ; = –110 kJ

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$; ΔH –132 kJ

What is the mole composition of the mixture of steam and oxygen on being passed over coke at 1273 K, keeping temperature constant.

(A) 0.5:1 (B) 0.6:1 (C) 0.8:1 (D) 1:1

Solution

(B) The first reaction is exothermic and the second one is endothermic. If a mixture of steam and O_2 is passed over coke and temperature is constant, the conversion of each to CO should not show any heat change, that is, total heat evolved in I = total heat absorbed in II.

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$$n_1 \times 2 \times 110 = n_2 \times 132$$

Therefore, $$\frac{n_1}{n_2} = \frac{132}{200} = \frac{0.6}{1}$$

15. For a reaction, A + B → AB, ΔC_p is given by the equation $40 + 5 \times 10^{-3}\ T$ J K^{-1} in the temperature range 300–600 K. The enthalpy of the reaction at 300 K is –25.0 kJ. Calculate the enthalpy of the reaction at 450 K. Also $S°(NO_2)$ – 57.5 cal deg^{-1}, $S°(O_2)$ – 49.0 cal deg^{-1}, $S°(NO)$ = 50.3 cal deg^{-1}, $S°(O_3)$ = 56.8 cal deg^{-1}.

(A) –10.12 kJ (B) –28.32 kJ (C) –18.72 kJ (D) –8.21 kJ.

Solution

(C) According to Kirchhoff's equation,

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_p \, dT = -25000 + \int_{300}^{450} (40 + 5\times10^{-3}\ T)dT = -18.72 \text{ kJ}$$

16. The enthalpy of neutralization of HCl by NaOH is −55.9 kJ mol^{-1}. If the enthalpy of neutralization of HCN by NaOH is −12.1 kJ mol^{-1}, the enthalpy of dissociation of HCN is

(A) −43.8 kJ (B) 43.8 kJ (C) 68 kJ (D) −68 kJ

Solution

(B) $\text{HCl} + \text{NaOH} \longrightarrow \text{NaCl} + \text{H}_2\text{O} \quad \Delta H_1 = -55.9 \text{ kJ mol}^{-1}$

$\text{HCN} + \text{NaOH} \longrightarrow \text{NaCN} + \text{H}_2\text{O} \quad \Delta H_2 = -12.1 \text{ kJ mol}^{-1}$

Enthalpy of dissociation of HCN = $\Delta H_2 - \Delta H_1$ = –12.1 – (–55.9) = +43.8 kJ

17. Which of the reaction defines ΔH_f°?

(A) $\frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{F}_2(g) \rightarrow \text{HF}(g)$

(B) $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g)$

(C) $\underset{\text{Diamond}}{\text{C}} + \text{O}_2(g) \rightarrow \text{CO}_2(g)$

(D) $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$

Solution

(A) ΔH_f° is the enthalpy of formation; in standard state of 1 mol of a substance form its constituent elements in their standard states, for example, $\frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{F}_2(g) \rightarrow \text{HF}(g)$.

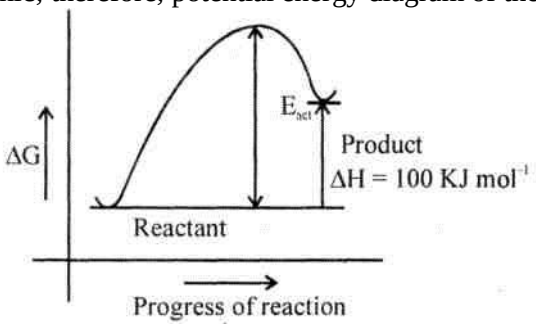
18. If ΔH of a reaction is 100 kJ mol^{-1}, then the activation energy must be

(A) greater than 100 kJ mol^{-1} (B) less than 100 kJ mol^{-1}

(C) equal to 100 kJ mol^{-1} (D) none of these.

Solution

(A) The reaction is endothermic; therefore, potential energy diagram of the given reaction is



$$\Delta H = \Sigma H_P - \Sigma H_R = 100$$

Thyerefor, from the figure, we can say that E_{act} > 100 kJ mol^{-1}.

19. Heat of hydrogenation of ethene is x_1 and that of benzene is x_2. Hence, resonance energy is

(A) $x_1 - x_2$ (B) $x_1 + x_2$ (C) $3x_1 - x_2$ (D) $x_1 - 3x_2$

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Solution
(C) $C_6H_6 + H_2 \rightarrow C_6H_{12}$ $\Delta H = x_2$
$3C_2H_4 + 3H_2 \rightarrow 3C_2H_6$ $\Delta H = x_1$
Therefore, resonance energy of benzene (containing three double bonds) = $3x_1 - x_2$.

20. Heat of neutralization of oxalic acid is –25.4 k cal mol^{-1} using strong base, NaOH. Hence, enthalpy change of the process is $H_2C_2O_4 \rightleftharpoons 2H^+ + C_2O_4^{2-}$ is
(A) 2.0 kcal (B) –11.8 kcal (C) 1.0 kcal (D) –1.0 kcal
Solution
(A) The heat of neutralisation of strong acid and strong base = –13.7 kcal equiv^{-1}.
Therefore, –13.7 × 2 = –27.4 kcal should be evolved, but evolved actually is –25.4 kcal. Therefore,

$$\Delta_{diss}H = -25.4 - (-27.4) = +2 \text{ kcal}$$

21. The lattice energy of NaCl is –780 kJ mol$^{-1.}$ The enthalpies of hydration of Na^+(g) and Cl^-(g) ions are –406 kJ mol^{-1} and –364 kJ mol^{-1}. The enthalpy of solution of NaCl(s) is
(A) 738 kJ mol^{-1} (B) 10 kJ mol^{-1}(C) –10 kJ mol^{-1} (D) –822 kJ mol^{-1}
Solution
(B) $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$ ΔH = +780 kJ (Lattice energy)
$Na^+(g) + aq \rightarrow Na^+(aq)$ ΔH = –406 kJ (Hydration)
$Cl^-(g) + aq \rightarrow Cl^-(aq)$ ΔH = –364 kJ (Hydration)
The net reaction is dissolution of NaCl(s)

$$NaCl(s) + 2H_2O \rightarrow Na^+(aq) + Cl^-(aq) \qquad \Delta H_{solution} = 780 - (406 + 364) = 10 \text{ kJ mol}^{-1}$$

22. Some of the thermodynamic parameters are state variables, while some are process variables. Some groups of the parameters are given. Choose the correct one.
(A) State variables: Temperature, Number of moles
Process variables: Internal energy, work done by the gas
(B) State variables: Volume, temperature
Process variables: Internal energy, work done by the gas
(C) State variables: work done by the gas, heat rejected by the gas.
Process variables: Temperature, volume
(D) State variables: Internal energy, volume
Process variables: Work done by the gas, heat absorbed by the gas
Solution
(D) Internal energy and volume depend on initial and final states.

23. Using only the following data:
(I) $Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(s) + 3CO_2(g); \quad \Delta H^o = -26.8 \text{ kJ}$
(II) $Fe(s) + CO(g) \rightleftharpoons FeO(s) + CO(g); \quad \Delta H^o = +16.5 \text{kJ}$
the $\Delta H°$ value, in kilojoules, for the reaction $Fe_2O_3(s) + CO(g) \rightarrow 2FeO(s) + CO_2(g)$ is calculated as
(A) –43.3 (B) –10.3 (C) +6.2 (D) +10.3
Solution
(C) Multiplying Eq. (II) by 2 and adding to Eq. (I) gives the required reaction with $\Delta H°$ = –26.8 + 2(+16.5) = +6.2 kJ.

24. The Kirchhoff's equation gives the effect of ____ on heat of reaction.

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(A) pressure (B) temperature (C) volume (D) molecularity

Solution

(B) Kirchhoff's equation is: $\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$

25. One mole of a real gas is subjected to heating at constant volume from (p_1, V_1, T_1) state to (p_2, V_2, T_2) state. Then it is subjected to irreversible adiabatic compression against constant atmosphere till the system reaches the final state (p_3, V_3, T_3). If the constant volume molar heat capacity of real gas is C_V. Find out the correct expression for ΔH from state 1 to state 3.

(A) $C_V(T_3 - T_1) + (p_3V_1 - p_1V_1)$ (B) $C_V(T_2 - T_1) + (p_3V_2 - p_1V_1)$

(C) $C_V(T_2 - T_1) + (p_3V_1 - p_1V_1)$ (D) $C_p(T_2 - T_1) + (p_3V_1 - p_1V_1)$

Solution

(C) $\Delta H_A = C_V(T_2 - T_1) + (p_2V_1 - p_1V_1)$

$\Delta H_B = \Delta U + p_3V_2 - p_2V_1 = p_3(V_2 - V_1) + p_3V_2 - p_2V_1 = p_3V_1 - p_2V_1$

$\Delta H_{overall} = \Delta H_A + \Delta H_B = C_V(T_2 - T_1) + (p_3V_1 - p_1V_1)$

26. In which case of mixing of a strong acid and a base, each of 1(N) concentration, temperature increase is the highest?

(A) 20 mL acid and 30 mL alkali (B) 10 mL acid and 40 mL alkali

(C) 25 mL acid and 25 mL alkali (D) 35 mL acid and 15 mL alkali

Solution

(C) When 25 mL acid is reacting with 25 mL of alkali, maximum equivalent of acid is reacting with alkali since the volume of the resulting solution is the same in every cases; therefore, increase in temperature is the highest where maximum equivalents of acids and alkalies are reacting (limiting reagent should be taken in account).

27. The molar entropy of vaporization of acetic acid is 14.4 cal K^{-1} mol^{-1} at its boiling point 118°C. The latent heat of vaporization of acetic acid is

(A) 49 cal g^{-1} (B) 64 cal g^{-1} (C) 94 cal g^{-1} (D) 84 cal g^{-1}

Solution

(C) $\Delta S = \dfrac{\Delta H}{T(K)} \Rightarrow 14.4 = \dfrac{\Delta H}{391} \Rightarrow \Delta H = 391 \times 14.4 = 5630 \text{ cal mol}^{-1} = \dfrac{5630}{60} = 93.8 \text{ cal g}^{-1}$

28. The bond energies of C≡C, C–H, H–H, and C=C are 198, 98, 103, and 145 kcal, respectively. The enthalpy change of the reaction $HC \equiv CH + H_2 \rightarrow C_2H_4$ is

(A) 48 kcal (B) 96 kcal (c) –40 kcal (D) –152 kcal

Solution

(C)

Enthalpy of reaction = ΣBond energies of Reactants – Σ Bond energies of Products

Therefore,

$$\Delta H = [2(C-H) + (C \equiv C) + (H-H)] - [4(C-H) + (C=C)]$$
$$= [2(98) + 198 + 103] - [4(98) + 145] = -40 \text{ kcal}$$

29. During the isothermal mixing of ideal gases at pressure p, the entropy change per mole for the mixing process is $-R\Sigma x_i \ln x_i$ where x_1, x_2, … x_i are the mole fractions of the components, 1, 2, …, i of the mixture. Assuming ideal gas behavior, calculate ΔS for the mixing of 0.8 mol of N_2 and 0.2 mol of O_2 (at 25°C and 0.9 atm) [1 eu = cal deg^{-1}]

(A) 0.9943 eu (B) 0.7533 eu (C) 0.6798 eu (D) 0.7112 eu

Solution

(A) Mole fractions are 0.8 and 0.2. Therefore, the entropy of mixing per mole is

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$$\Delta S_{mix} = -1.987[0.8 \ln(0.8) + 0.2 \ln(0.2)] = -1.987[-0.1785 - 0.3219] = 0.9943 \text{ eu}$$

30. When 1 mol of an ideal gas to 20 atm pressure and 15 L volume expands such that the final pressure becomes 10 atm and the final volume becomes 60 L. Calculate entropy change for the reaction ($C_{p,m}$ = 30.96)

(A) 802 J K^{-1} mol^{-1} (B) 62.42 kJ K^{-1} mol^{-1}

(C) 120 × 10^2 J K^{-1} mol^{-1} (D) 27.22 J K^{-1} mol^{-1}

Solution

(D) $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$; $\frac{T_2}{T_1} = \frac{6}{3}$

$$\Delta S = 2.303 \times n\left\{C_p \log_{10}\frac{T_2}{T_1} + R\log_{10}\frac{p_1}{p_2}\right\} = 2.303 \times 1\left\{30.96 \log_{10}\frac{6}{3} + R\log_{10}\frac{20}{10}\right\} = 27.22 \text{ J K}^{-1}\text{ mol}^{-1}$$

31. The dissociation energies of CH_4 and C_2H_6 are, respectively, 360 and 620 kcal mol^{-1}. The bond energy of C–C is

(A) 260 kcal mol^{-1} (B) 180 kcal mol^{-1} (C) 130 kcal mol^{-1} (D) 80 kcal mol^{-1}

Solution

(D) $CH_4 \rightarrow C(s) + 2H_2(g)$; ΔH = 360 kcal

$C_2H_6 \rightarrow 2C(s) + 3H_2(g)$; ΔH = 620 kcal

The average C–H bond energy = $\frac{360}{4} = 90$ kcal

Therefore, C–C bond energy = 620 – 90 × 6 = 620 – 540 = 80 kcal

32. The enthalpy change of the reaction $Al_2Cl_6(s) + 6Na(s) \rightarrow 2Al(s) + 6NaCl(s)$ is –257 kcal. Given that the heat of formation of NaCl(s) is –98.0 kcal, then the heat of formation of $Al_2Cl_6(s)$ is

(a) 158 kcal (b) –331 kcal (c) –166 kcal (d) 316 kcal

Solution

(B) $\Delta_r H = 6\Delta H^o_{f(NaCl)} - \Delta H^o_{f(Al_2Cl_6)}$

where $\Delta H^o_{f(NaCl)}$ and $\Delta H^o_{f(Al_2Cl_6)}$ are the heats of formation of NaCl and Al_2Cl_6. For Al(s) and Na(s), $\Delta H^o_f = 0$. Therefore, $\Delta H^o_{f(Al_2Cl_6)} = -331$ kcal .

33. The heat of neutralization of HCl by NaOH is –55.9 kJ mol^{-1}. If the heat of neutralization of HCN by NaOH is –12.1 kJ mol^{-1}, then the energy of dissociation of HCN is

(A) –43.8 kJ (B) 43.8 kJ (C) 68 kJ (D) –68 kJ

Solution

(B) The heat of neutralization = – 55.9 kJ. Now,

the heat of neutralization of HCN by NaOH = the heat released on neutralization + the energy of dissociation of HCN = –12.1 kJ

So, the energy of dissociation of HCN = + 55.9 – 12.1 = 43.8 kJ

This is because HCN is a weak acid.

34. The temperature of 5 mL of a strong acid increases by 5°C when 5 mL of a strong base is added to it. If 10 mL of each is mixed, temperature should increase by

(A) 5°C (B) 10°C (C) 15°C (D) cannot be predicted.

Solution

(A) When 5 mL of strong acid reacting with 5 mL of strong base, net heat evolved = ΔH. Therefore,

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$$\text{Temperature increase} = \frac{\Delta H}{ms} \text{ as } \Delta H = ms\Delta T$$

where m is the mass of the material, s is its specific heat capacity and ΔT is the change in its temperature.

When 10 mL of each are reaction, the heat evolved = $2\Delta H$ and mass of the solution = $2m$

So, the temperature increase $= \frac{2\Delta H}{2ms} = \frac{\Delta H}{ms}$

35. For a reaction at equilibrium,

(A) $\Delta G = \Delta G° = 0$ (B) $\Delta G = 0$ but not $\Delta G°$

(C) $\Delta G° = 0$ but not ΔG (D) $\Delta G = \Delta G° \neq 0$

Solution

(B) For a reaction at equilibrium $\Delta G = 0$ and not $\Delta G°$. $\Delta G = \Delta G°$, $\Delta G = \Delta G° + RT \ln Q$ at equilibrium, $\Delta G = 0$ and $\Delta G° = -RT \ln K_{eq}$.

36. Among the following, the reaction for which $\Delta H = \Delta U$ is

(A) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ (B) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

(C) $C_2H_5OH(l) + 3O_2(g) \rightleftharpoons 2CO_2(g) + 3H_2O(l)$ (D) $C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g)$

Solution

(B) When $\Delta n = 0$, $\Delta H = \Delta U$ because $\Delta H = \Delta U + \Delta n_g RT$. In the other three cases, $\Delta n_g \neq 0$.

37. The heats of neutralization of four acids A, B, C, D are –13.7, –9.4, –11.2, and –12.4 kcal, respectively, when they are neutralized by a common base. The acidic character obeys the order

(A) A > B > C > D (B) A > D > C > B (C) D > C > B > A (D) D > B > C > A

Solution

(B) Lower is heat of neutralization, more is dissociation energy, weaker is acid. As some of the neutralization energy is spend in making that weak acid dissociated.

38. For the reaction, $2N_2(g) + O_2(g) \rightarrow 2N_2O$, at –298K ΔH is 164 kJ mol^{-1}. The ΔU of the reaction is

(A) 166.5 kJ mol^{-1} (B) 161.5 kJ mol^{-1} (C) 164.0 kJ mol^{-1} (D) 169 kJ mol^{-1}

Solution

(A) $\Delta H = \Delta U + \Delta nRT$ where $\Delta n = 2 - 3 = -1$. Substituting given values, we get

$$164000 = \Delta E - 1 \times 8.314 \times 298$$

or $\Delta U = 164000 + 2477.5 = 166.5$ kJ mol^{-1}

39. Enthalpy of fusion of a liquid is 1.435 kcal mol^{-1} and molar entropy change is 5.26 cal mol^{-1}K^{-1}. Hence, the melting point of liquid is

(A) 100°C (B) 0°C (C) 373 K (D) –273°C

Solution

(B) $\Delta S = \frac{\Delta H}{T} \Rightarrow T = \frac{\Delta H}{\Delta S} = \frac{1435 \text{ cal}}{5.26} = 273 \text{ K} = 0°\text{C}$

40. 1 mol of NH_3 gas at 27°C is expanded under adiabatic conditions to make volume 8 times (γ = 1.33). Final temperature and work done, respectively, are

(A) 150 K, 900 cal (B) 150 K, 400 cal (C) 250 K, 1000 cal (D) 200 K, 800 cal

Solution

(A) Temperature and volume are related for adiabatic process as: $T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1}$. Therefore,

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$$T_2 = \frac{T_2 V_2^{\gamma-1}}{V_2^{\gamma-1}} = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 300\left(\frac{1}{8}\right)^{1/3} = 300 \times \frac{1}{2} = 150 \text{ K}$$

Also, $\frac{C_p}{C_V} = \gamma = \frac{4}{3}$ and $C_p - C_V = R$. Solving, we get $C_p = 4R$ and $C_V = 3R$

Therefore, adiabatic work done is

$$\Delta w = -C_V \Delta T = -3 \times 2 \times (150 - 300) = 900 \text{ cal}$$

41. The gas absorbs 100 J heat and is simultaneously compressed by a constant external pressure of 1.50 atm from 8 L to 2 L in volume. Hence, ΔU will be:

(A) –812 J (B) 812 J (C) 1011 J (D) 911 J

Solution

(C) $\Delta H = \Delta U + p\Delta V \Rightarrow 100 = \Delta E + 1.5(2-8) \times \frac{8.314}{0.0821} \Rightarrow \Delta E = 1011.4$ J

42. An ideal gas can be expanded from an initial state to a certain volume through two different processes, (I) $pV^2 = K$ and (II) $p = KV^2$, where K is a positive constant. Then, choose the correct option from the following:

(A) Final temperature in (I) will be greater than in (II).
(B) Final temperature in (II) will be greater than in (I).
(C) Work done by the gas in both the processes would be equal.
(D) Total heat given to the gas in (I) is greater than in (II).

Solution

(B) Process (I): $pV^2 = K \Rightarrow \frac{nRT}{V}V^2 = K \Rightarrow TV = \text{constant} \Rightarrow T \propto \frac{1}{V}$

Process (II): $p = KV^2 \Rightarrow \frac{nRT}{V} = KV^2 \Rightarrow \frac{T}{V^3} = \text{constant} \Rightarrow T \propto V^3$

43. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta H_{H-H} = x_1$; $\Delta H_{O-O} = x_2$ and $\Delta H_{O-H} = x_3$. The latent heat of vaporization of water liquid into water vapor = x_4, then ΔH_f^o (heat of formation of liquid water) is

(A) $x_1 + \frac{x_2}{2} - x_3 + x_4$ (B) $2x_3 - x_1 - \frac{x_2}{2} + x_4$ (C) $x_1 + \frac{x_2}{2} - 2x_3 - x_4$ (D) $x_1 + \frac{x_2}{2} - 2x_3 + x_4$

Solution

(C)

For the reaction $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$, the enthalpy of reaction will be given by

$$\Delta H_{(g)} = \sum \text{BE (Reactants)} - \sum \text{BE (Products)} -$$

$$= \left[\text{BE (H – H)} + \frac{1}{2}\text{BE (O – O)}\right] - \left[2\text{BE (O – H)}\right]$$

$$\Delta H_{(g)} = x_1 + \frac{x_2}{2} - 2x_3$$

For formation of liquid water, the heat of latent heat for conversion of water vapor into liquid water needs to be added. This value is equal to –(latent heat of vaporization), so enthalpy of formation of liquid water is

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$$\Delta H_{(l)} = x_1 + \frac{x_2}{2} - 2x_3 - x_4$$

44. The intermediate SiH_2 is formed in the thermal decomposition of silicon hydrides. Calculate ΔH_f° of SiH_2 with the help of following reactions

Si_2H_6 (g) + H_2(g) → 2SiH_4(g); $\Delta H° = -11.7$ kJ mol^{-1}

SiH_4 (g) → SiH_2 (g) + H_2 (g); $\Delta H° = +239.7$ kJ mol^{-1}

(Given ΔH_f of Si_2H_6 (g) = + 80.3 kJ mol^{-1})

(A) 353 kJ mol^{-1} (B) 321 kJ mol^{-1} (C) 198 kJ mol^{-1} (D) 274 kJ mol^{-1}

Solution

(D) For the first reaction,

$$Si_2H_6\,(g) + H_2(g) \rightarrow 2SiH_4(g); \quad \Delta H° = -11.7 \text{ kJ mol}^{-1}$$

Given that ΔH_f of Si_2H_6 (g) = + 80.3 kJ mol^{-1}. Let ΔH_f of H_2(g) = x, and ΔH_f of SiH_2(g) = y. Therefore,

$$2x - 80.3 = -11.7 \Rightarrow 2x = 80.3 - 11.7 = 68.6 \text{ kJ mol}^{-1} \Rightarrow x = 34.3 \text{ kJ mol}^{-1}$$

For the second reaction

$$SiH_4(g) \rightarrow SiH_2(g) + H_2(g); \qquad \Delta H = +239.7 \text{ kJ mol}^{-1}$$

Therefore,

$$y - 34.3 = 239.7 \Rightarrow y = (239.7 + 34.3) \text{ kJmol}^{-1} = 274 \text{ kJ mol}^{-1}$$

45. The enthalpies of the following reactions are shown along with

$\frac{1}{2}H_2(g) + O_2(g) \rightarrow OH(g)$; $\Delta H = 42.09$ kJ mol^{-1}

$H_2(g) \rightarrow 2H(g)$; $\Delta H = 435.89$ kJ mol^{-1}

$O_2(g) \rightarrow 2O(g)$; $\Delta H = 495.05$ kJ mol^{-1}

Calculate the O–H bond energy for the hydroxyl radical,

(A) 223.18 kJ mol^{-1} (B) 423.38 kJ mol^{-1} (C) 513.28 kJ mol^{-1} (D) 113.38 kJ mol^{-1}

Solution

(B) We have to calculate the enthalpy of the reaction

$$OH(g) \rightarrow O(g) + H(g)$$

From the given reactions, this can be obtained as follows.

$$-\left[\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \rightarrow OH(g)\right]; \Delta H = -42.09 \text{ kJ mol}^{-1}$$

$$+\frac{1}{2}[H_2(g) \rightarrow 2H(g)] \quad ; \Delta H = \frac{1}{2} \times 435.89 \text{ kJ mol}^{-1}$$

$$+\frac{1}{2}[O_2(g) \rightarrow 2O(g)] \quad ; \Delta H = \frac{1}{2} \times 495.05 \text{ kJ mol}^{-1}$$

Adding, we get

$$OH(g) \rightarrow H(g) + O(g); \Delta H = 423.38 \text{ kJ mol}^{-1}$$

46. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of CO_2(g), H_2O(l) and propene (g) are –393.5, –285.8, and 20.42 kJ mol^{-1}, respectively. The enthalpy of isomerization of cyclopropane to propene is –33.0 kJ mol^{-1}.

(A) –1021.32 kJ mol^{-1} (B) –2091.32 kJ mol^{-1} (C) –5021.32 kJ mol^{-1} (D) –3141.32 kJ mol^{-1}

Solution

(B) For the reaction

$$CH_3CH{=}CH_2(g) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l) \qquad (1)$$

$\Delta_r H = 3\Delta H_f(CO_2, g) + 3\Delta H_f(H_2O, l) - \Delta H_f(CH_3CH{=}CH_2) = [3(-393.5) + 3(-285.8) - (20.42)]$ kJmol^{-1}

$= -2058.32$ kJ mol^{-1}

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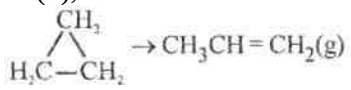
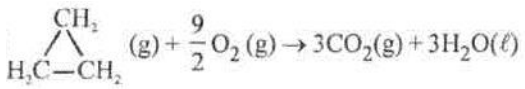
To the reaction (1), if we add the reaction



$\Delta H = -33.0$ kJ mol^{-1}

we get



Hence, $\Delta_c H$(cyclopropane) = (– 2058.32 – 33.0) kJ mol^{-1} = –2091.32 kJ mol^{-1}

47. In thermodynamics, a process is called reversible when
(A) surroundings and system change into each other.
(B) there is no boundary between system and surroundings.
(C) the surroundings are always in equilibrium with the system.
(D) the system changes into the surroundings spontaneously.
Solution
(C) In a reversible process, the driving force and opposing force of that process are nearly equal, and hence, the system and the surrounding always remain in equilibrium with each other.

48. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) → (4.0 atm, 5.0 L, 245 K) with a change in internal energy, ΔU = 30.0 L atm. The change in enthalpy in the process in liter atm is
(A) 40.0 (B) 42.3 (C) 44.0 (D) not defined, because pressure is not constant.
Solution
(C) $\Delta H = \Delta U + p\Delta V = 30 + (4 \times 5) - (2 \times 3) = 44$ L atm

49. Find temperature of vapor at 1 atm. Given that ΔH = 30 kJ mol^{-1} and ΔS = 75 J K^{-1} mol^{-1}.
(A) 400 K (B) 350 K (C) 298 K (D) 250 K
Solution
(A) $\Delta S = \dfrac{\Delta H}{T} \Rightarrow T = \dfrac{30 \times 10^3}{75} = 400$ K

50. Two separate experiments were carried out involving adiabatic reversible expansion, taking monoatomic gas in one case and a diatomic gas in the second case. In each case, the initial temperature was T_i and expansion was from volume V_1 to volume V_2. The final temperatures attained were T_M for monoatomic gas and T_D for diatomic gas. Then
(A) $T_M = T_D < T_i$ (B) $T_M < T_D < T_i$ (C) $T_D > T_M > T_i$ (D) $T_D < T_M < T_f$
Solution
(B) For adiabatic expansion,

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Now, γ = 1.66 for monoatomic gas and 1.40 for diatomic gas. Hence, for monoatomic gas,

$$\frac{T_M}{T_i} = \left(\frac{V_1}{V_2}\right)^{0.66}$$

and for diatomic gas,

$$\frac{T_D}{T_i} = \left(\frac{V_1}{V_2}\right)^{0.40}$$

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As $\frac{V_1}{V_2} < 1$ (since $V_2 > V_1$) $\Rightarrow \frac{T_M}{T_i} < 1 \Rightarrow T_M < T_i$

and $\frac{T_D}{T_i} < 1 \Rightarrow T_D < T_i$

Suppose $V_2 = 10\ V_1$. Then,

$$\frac{T_M}{T_D} = \left(\frac{1}{10}\right)^{0.66-0.40} = \left(\frac{1}{10}\right)^{0.26}$$

or $T_M < T_D$. Hence, $T_M < T_D < T_i$.

Multiple Correct Choice Type

1. Which of the following statement(s) is/are correct?

(A) The system of constant entropy and constant volume will attain the equilibrium in a state of minimum energy

(B) The entropy of the universe is increasing.

(C) The process would be spontaneous when $(\Delta S)_{U,V} < 0$, $(\Delta U)_{S,V} > 0$

(D) The process would be spontaneous when $(\Delta S)_{U,V} > 0$, $(\Delta U)_{S,V} < 0$

Solution

(A, B, D) For a spontaneous process in an isolated system, $\Delta S_{U,V} > 0$. For a reversible adiabatic process, $\Delta S_{U,V} = 0$.

2. One mole of an ideal diatomic gas (C_V = 5 cal) was transformed from initial 25°C and 1 L to the state when temperature is 100°C and volume 10 L. Then for this process (R = 2 cal mol^{-1} K^{-1}) (take calories as unit of energy and kelvin for temperature)

(A) $\Delta H = 525$ (B) $\Delta S = 5 \ln \frac{373}{298} + 2 \ln 10$

(C) $\Delta U = 525$ (D) ΔG of the process cannot be calculated using given information.

Solution

(A, B) $\Delta S = nC_V \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right) = 5 \ln\left(\frac{373}{298}\right) + 2 \ln 10$

Also, $C_p - C_V = R \Rightarrow C_p = 7$. Now,

$$\Delta H = nC_p\Delta T = 1 \times 7 \times 75 = 525 \text{ cal}$$

and $\Delta U = nC_V\Delta T = 1 \times 5 \times 75 = 375$ cal

3. For an ideal gas

(A) $\left(\frac{\partial U}{\partial T}\right)_p = 0$ (B) $\left(\frac{\partial U}{\partial T}\right)_V = 0$ (C) $\left(\frac{\partial U}{\partial p}\right)_T = 0$ (D) $\left(\frac{\partial U}{\partial V}\right)_T = 0$

Solution

(C, D) According to the properties of ideal gases

$$\left(\frac{\partial E}{\partial P}\right)_T = \left(\frac{\partial E}{\partial V}\right)_T = 0$$

4. When a solid melts there will be

(A) an increase in enthalpy. (B) a decrease in free energy.

(C) no change in enthalpy. (D) a decrease in internal energy.

Solution

(A, B) Melting is an endothermic process.

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5. Variation of heat of reaction with temperature is given by Kirchhoff's equation, which is:

(A) $\Delta H_2 = \Delta H, + \Delta C_p(T_2 - T_1,)$ (B) $\frac{\Delta H_2 - \Delta H_1}{\Delta T} = \Delta C_p$

(C) $\frac{d(\Delta H)}{\Delta T} = \Delta C_p$ (D) None of these

Solution

(A, B, C) All the above forms are different ways of expressing Kirchhoff's equation.

6. When a real gas expands adiabatically against a finite pressure,

(a) its internal energy increases. (B) its internal energy decreases.

(C) its temperature always decreases. (D) its entropy always remains constant.

Solution

(B, C, D) $\Delta H = \Delta U + \Delta w$. If $\Delta H = 0$, $\Delta w = -\Delta U$. Thus, internal energy decreases. The temperature of the reversible adiabatic process always decreases, and is also known as isoentropic process.

7. Which of the following processes have positive value for ΔH?

(A) $H_2(g) \rightarrow 2H(g)$ (B) $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

(C) $H(g) \rightarrow H^+(g) + e^-$ (D) $H_2O(l) \rightarrow H_2O(s)$

Solution

(A, C) If the stability of products is lesser than that of reactants, then reactions will be endothermic and ΔH will be positive (as $\Delta H = \Sigma H_P - \Sigma H_R$).

8. $C(s) + \frac{1}{2}O_2 \rightarrow CO(g)$; $\Delta H° = -26$ kcal mol^{-1}

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$; $\Delta H° = -68$ kcal mol^{-1}

Which is/are correct statement(s)?

(A) Heat of formation of CO_2 is –68 kcal mol^{-1} (B) Heat of combustion of C(s) is –26 kcal mol^{-1}

(C) Heat of combustion of CO(g) –68 kcal mol^{-1} (D) Heat of formation of CO(g) is –26 kcal mol^{-1}

Solution

(C, D) Heat of combustion is the amount of heat released when 1 mol of that substance burns in excess of air.

9. An adiabatic process involves

(A) no exchange of heat.

(B) exchange of heat with change in volume.

(C) work done equal to change in internal energy.

(D) increase in temperature of the system under reversible compression.

Solution

(A, B, C) Adiabatic means no exchange of heat energy from the surrounding.

$\Delta U = q + w$. When $q = 0$, $\Delta U = w$.

10. Figure 7.40 illustrates the energy change of a set of reactions.

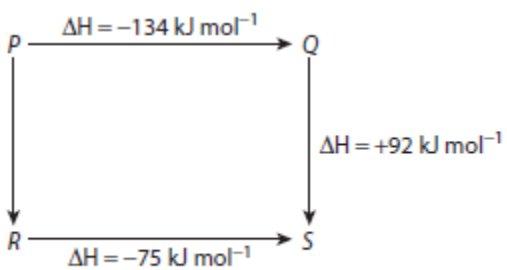

Figure 7.40

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Which of the following statements are correct?
(A) The enthalpy change for the reaction P → R is −33 kJ mol^{-1}.
(B) The enthalpy change for the transformation R → Q will be endothermic.
(C) The enthalpy change for the transformation R → Q will be exothermic.
(D) The enthalpy change for the transformation S → P will be +42 kJ mol^{-1}.

Solution

(C, D) $\Delta H_{PR} = \Delta H_{PQ} + \Delta H_{QS} + \Delta H_{SR} = (-134) + 92 - (-75) = +33$ kJ mol^{-1}

$\Delta H_{RQ} = \Delta H_{RS} + \Delta H_{SQ} = (-750) - (+92) = -167$ kJ $mol^{-1} \Rightarrow \Delta H_{RQ} < 0$, so exothermic.

$\Delta H_{SP} = \Delta H_{SQ} + \Delta H_{QP} = -(+92) - (-134) = +42$ kJ mol^{-1}

11. Which of the following process take(s) place with decrease in entropy?
(A) $3CO_2(g) \rightarrow 2O_3(g)$ (B) Sugar + Water → Solution
(C) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ (D) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

Solution

(A, C) In both reactions, large number of molecules combine together to form lesser number of molecules.

12. Choose the incorrect combination(s).

ΔH	ΔS	**Temperature (*T*)**	**Spontaneity**
(A) +	–	Any T	Non-spontaneous
(B) –	–	Low T	Non-spontaneous
(C) +	+	Low T	Spontaneous
(D) –	+	Any T	Spontaneous

Solution

(B, C)

ΔH	ΔS	Temperature (T)	Spontaneity
(B) –	–	Low T	Spontaneous
(C) +	+	Low T	Non-spontaneous

13. Mark out the correct one(s) about the pV plot system shown in Fig. 7.41

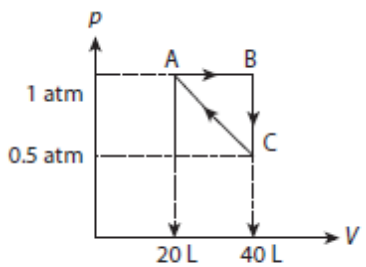

Figure 7.41

(A) The entropy change for the overall process is 0 (zero).
(B) $\Delta H > \Delta U$ for the overall process.
(C) Total work, $w = q$.

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(D) Total work = −620.77 J.
Solution
(A, D) The overall process is cyclic.
Thus, $\Delta U = 0$, $\Delta H = 0$, $\Delta S = 0$.
Now, $\Delta U = q + w \Rightarrow 0 = q + w \Rightarrow q = -w$
Total work = $w_{AB} + w_{BC} + w_{CA}$

$$w = -p(V_B - V_A) + 0 + 2.303 \times nRT \log \frac{V_C}{V_A}$$

$$= -1 \times (40 - 20) + 0 + 2.303 \times p_A V_a \log \frac{V_C}{V_A}$$

$$= -6.13 \text{ L atm} = -621.1 \text{ J}$$

(as 1 L atm = 101.325 J)

14. Which of the following statements are correct?
(a) When $\Delta G = 0$, the system is at equilibrium.
(b) When $\Delta G < 0$, the process will be spontaneous.
(c) When ΔG is negative, the process is said to be exergonic.
(d) When ΔG is positive, the process is said to be endergonic.
Solution
(A, B, C, D) $\Delta G = 0$ indicates that the system is at equilibrium and ΔG is negative for all spontaneous processes.
Exergonic process will occur spontaneously and is thermodynamically favorable.
Enodergonic processes are not spontaneous at standard conditions of pressure, temperature.

Assertion–Reasoning Type
Choose the correct option from the following:
(A) Statement 1 is True, Statement 2 is True; Statement 2 is a correct explanation for Statement 1.
(B) Statement 1 is True, Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1.
(C) Statement 1 is True, Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.
1. Statement 1: If a system goes from state A to state B by following reversible and irreversible process respectively then change in internal energy in both the process should be same.
Statement 2: Change in internal energy is a state function.
Solution
(A)
2. Statement 1: As solid changes to liquid and then to vapor state, entropy increases.
Statement 2: As going from solid to liquid and then to vapor state, disorder increases.
Solution
(A)
3. Statement 1: Entropy of all elements is zero at 0 K.
Statement 2: Standard entropy of all elements is greater than zero.
Solution
(A) Entropy of all elements and compounds decreases with decrease of temperature and becomes zero at 0 K.
4. Statement 1: Internal energy of a system is an extensive property.
Statement 2: The internal energy of a system depends upon the amount and physical state of the substance
Solution
(A)

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5. Statement 1: For an adiabatic process pV^{γ} = constant, where γ is the ratio of C_p and C_V)
Statement 2: The slope of isothermal process curve = $\gamma \times$ Slope of adiabatic curve
Solution
(C) Slope of isothermal process curve = slope of adiabatic process curve

6. Statement 1: The temperature of a gas does not change when it undergoes an adiabatic expansion.
Statement 2: During an adiabatic expansion of a real gas, the internal energy of the gas remains constant.
Solution
(D) During an adiabatic expansion of a real gas, the temperature of the gas changes and the internal energy of the gas falls.

7. Statement 1: If Gibbs energy change of the system is negative, the process is spontaneous even if the total Gibbs energy change of the system and the surroundings is positive.
Statement 2: The spontaneity of a process depends only on the Gibbs energy change of the system.
Solution
(A)
8. Statement 1: The standard free energies of all spontaneous occurring reactions are positive.
Statement 2: The free energies of elements standard states at 760 mm Hg and 298 K are taken as zero.
Solution
(D) Gibbs free energy is negative for spontaneous process.

9. Statement 1: The enthalpy of formation of $H_2O(l)$ is greater than that of $H_2O(g)$
Statement 2: Enthalpy change is negative for the condensation reaction : $H_2O(g) \rightarrow H_2O(l)$
Solution
(A)
10. Statement 1: The enthalpy of formation of gaseous oxygen molecules at 298 K and under a pressure of 1 atm is zero.
Statement 2: The entropy of formation of gaseous oxygen molecules under the same condition is zero.
Solution
(C) The entropy of formation of gaseous oxygen molecules is not zero.
11. Statement 1: The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.
Statement 2: The volume occupied by the molecules of an ideal gas is zero.
Solution
(D) Work done against vacuum is zero but heat absorbed may not be zero. The volume occupied by molecules of an ideal gas is negligible but not zero.
12. Statement 1: Heat energy is completely transformed into work during reversible isothermal expansion of an ideal gas.
Statement 2: During a reversible isothermal process of an ideal gas, the changes in internal energy due to decrease in pressure are nullified by the changes due to increase in volume.
Solution
(C) For isothermal expansion of ideal gas $\Delta U = 0$ and hence $q = -w$

Comprehension Type
Read the paragraphs and answer the questions that follow.
Paragraph I
Enthalpy of neutralization is defined as the enthalpy change when 1 mol of H^+ in dilute solution combines with 1 mol of OH^- to give rise to undissociated water, that is, $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

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$\Delta H = -57.54$ kJ mol^{-1} or -13.7 kcal mol^{-1}.When 1 mol of strong monoprotic acid is mixed with 1 mol of strong base, the above neutralization reaction takes place.
When a weak acid/base reacts with a strong base/acid, the release of heat is less than 57.54 kJ mol^{-1}. It is because of the fact that these acids/bases are not completely ionized in the solution. Some heat is consumed in ionizing them.

1. When 1 g equiv. of NaOH reacts with 0.33 g equiv. of HCl, enthalpy change is –4.6 cal. When 0.66 g equiv. of HCl is further added, enthalpy change would be

(A) –13.7 cal (B) –9.2 cal (C) 13.7cal (D) 9.2 cal

Solution

(B) The reaction involved is

	HCl	$+ NaOH$	$\rightarrow NaCl$	$+ H_2O$
Initial equivalent.	0.33	1	0	0
Equivalent at equilibrium	0	0.67	0.33	0.33
Equivalent added	0.66	0.01	0.66	0.66

$\Delta H = -4.6$ cal. On further addition $\Delta H = -9.2$ cal

2. In the following reaction involving neutralization of HF (a weak acid) with NaOH (a strong base).

$$HF\ (aq) + NaOH\ (aq) \rightarrow NaF(aq) + H_2O(l)$$

the heat of neutralization is –68.6kJmol^{-1}. This value is much higher than the heat of neutralization of strong acid with strong base (= –57.3 kJ mol^{-1}). This is because

(A) in aqueous solution, HF behaves as a strong acid.

(B) there is hydration of F^- ion in aqueous solution, and process is exothermic.

(C) both A and B.

(D) none of these.

Solution

(B)

The observed value of heat of neutralization of HF is more due to extensive solvation of F^- ion because of its small size. Hydration reactions are exothermic also in nature.

3. Heat of dissociation of CH_3COOH is 0.005 kcal g^{-1}; hence, enthalpy change when 1 mol of $Ca(OH)_2$ is completely neutralized by CH_3COOH is

(A) –27.4 kcal (B) –13.6 kcal (C) –26.8 kcal (D) –27.1 kcal

Solution

(D) $2CH_3COOH + Ca(OH)_2 \rightarrow (CH3COO)_2Ca + 2H_2O$

2 mol 1 mol

$\Delta_{diss}H$ of CH_3COOH = 0.005 kcal g^{-1} × 60 = 0.3 kcal mol^{-1}

Paragraph II

Enthalpy of reaction is the heat change accompanying any reaction, depending on the nature of the reaction the enthalpy of the reaction is named accordingly. For example, in the reaction

$$CH_4(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l);\ \Delta H = -890.4 \text{ kJ mol}^{-1}$$

This reaction shown that 890.4 kJ of heat is produced when methane is completely burnt is known as heat of combustion. For example, in the reaction

$$C(s) + O_2(g) \rightarrow CO_2(g);\ \Delta H = -393.5 \text{ kJ mol}^{-1}$$

when $CO_2(g)$ is formed from its elements, that is, from C(s) and $O_2(g)$ 393.5 kJ of heat is produced and the process in heat of formation.

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4. The enthalpy of formation of methane from the following data

(I) $C(s) + O_2(g) \rightarrow CO_2(g);\ \Delta H = -393.5\ \text{kJ mol}^{-1}$

(II) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l);\ \Delta H = -285.8\ \text{kJ mol}^{-1}$

(III) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890.4\ \text{kJ/mol}$

(A) -74.9 kJ mol^{-1} (B) 54.6 kJ mol^{-1} (C) 99.7 kJ mol^{-1} (D) -89.6 kJ mol^{-1}

Solution

(A) For the reaction

$$\Delta_r H = \Sigma H_f^o(\text{Product}) - \Sigma H_f^o(\text{Reactants})$$

$$-890.4 = [-393.7 + 2(-285.8)] - [\Delta H_f^o(CH_4) + 2(0)]$$

Therefore, $\Delta H_f^o(CH_4) = -965.3 + 890.4 - 74.9\ \text{kJ mol}^{-1}$

5. Calculate the enthalpy of formation of sucrose $(C_{12}H_{22}O_{12})n$ from the following data:

(I) $\Delta H = -5200.7$ kJ mol^{-1}

(II) $C(s) + O_2(g) \rightarrow CO_2(g);\ \Delta H = -393.5\ \text{kJ mol}^{-1}$

(III) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l);\ \Delta H = -285.8\ \text{kJ mol}^{-1}$

(A) -10.3 kJ mol^{-1} (B) +863.4 kJ mol^{-1} (C) -2677.1 kJ mol^{-1} (D) -4321.3 kJ mol^{-1}

Solution

(C) $\Delta H_{\text{reaction}} = \Sigma H_f^o(\text{Products}) - \Sigma H_f^o(\text{Reactants}) = -285.8\ \text{kJ mol}^{-1}$

$[11 \times (-285.8) + 12(-394.5)] - [12 \times 0 + \Delta H_f^o(\text{Sucrose})] = -5200.7$

Therefore, $(-3143.8 - 4734) - \Delta H_f^o(\text{Sucrose}) = -5200.7$

or $\Delta H_f^o = -2677.1\ \text{kJ mol}^{-1}$

6. Calculate the enthalpy of combustion of benzene from the following data:

(I) $6C(s) + 3H_2(g) \rightarrow C_6H_6(l)$, $\Delta H = 49.0$ kJ mol^{-1}

(II) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l);\quad \Delta H = -285.8\ \text{kJ mol}^{-1}$

(III) $C(s) + O_2(g) \rightarrow CO_2(g);\quad \Delta H = -389.3\ \text{kJ mol}^{-1}$

(A) +463.6 kJ mol^{-1} (B) +32.4 kJ mol^{-1} (C) -1432.3 kJ mol^{-1} (D) -3242.2 kJ mol^{-1}

Solution

(D) $C_6H_6(l) + 12O_2(g) \rightarrow 6CO_2(g) + 12\ H_2O(l)$

$$\Delta H_{\text{reaction}} = \Sigma \Delta H_f^o(\text{Products}) - \sum \Delta H_f^o(\text{Reactants})$$

$$= \left[6 \times (-398.3) + 12(-285.8)\right] - \left[49 + 12 \times 0\right]$$

$$= -3242.2\ \text{kJ mol}^{-1}$$

Paragraph III

Consider the following reaction $N_2O_4(g) \rightarrow 2NO_2(g)$. The Gibbs energy of the reaction occurring at 298 K and 1 atm has been plotted against the fraction of N_2O_4 dissociated as shown in Fig. 7.42.

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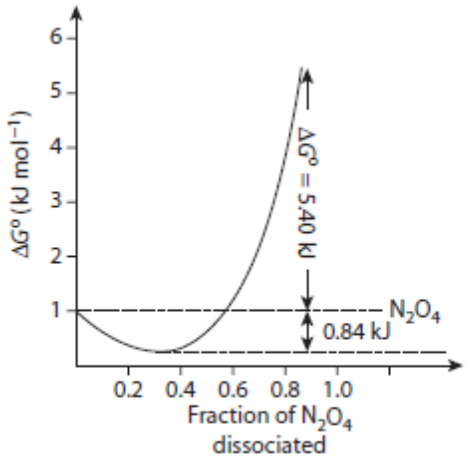

Figure 7.42

7. When 2 mol of NO_2 change into equilibrium mixture with N_2O_4, then $\Delta G°$ is

(A) −5.40 kJ (B) +5.40 kJ (C) −6.24 kJ (D) 6.24 kJ

Solution

(C) $\Delta G° = (-5.40) + (-0.84) = -6.24$ kJ.

8. When 1 mol of N_2O_4 changes into equilibrium mixture with NO_2, then $\Delta G°$ is

(A) −5.40 kJ (B) 0.84 kJ (C) −0.84 kJ (D) 6.24

Solution

(C) $\Delta G° = -0.84$ kJ

9. Select out the correct statement.

(A) The conversion of N_2O_4 into $2NO_2$ is spontaneous.

(B) The conversion of $2NO_2$ into N_2O_4 is non-spontaneous.

(C) The attainment of equilibrium from N_2O_4 and from NO_2 are both equally spontaneous.

(D) The attainment of equilibrium from 2 mol of NO_2 with N_2O_4 is more spontaneous than the conversion of $2NO_2$ into N_2O_4.

Solution

(D) $2NO_2 \rightleftharpoons N_2O_4 \quad \Delta G^\circ = -6.24\,\text{kJ}$

$2NO_2 \rightarrow N_2O_4 \quad \Delta G^\circ = -5.40\,\text{kJ}$

One reaction is in equilibrium other is not..

Integer Answer Type

The answer is a **non-negative integer**.

1. One mole of monatomic perfect gas, initially at 1.0 atm pressure and at 300 K is heated reversibly to 400 K at constant volume. Calculate the change in internal energy and the work done.

Solution

(0) For a monoatomic perfect gas $C_V = \frac{3}{2}R$

The change in internal energy, $\Delta E = C_V \Delta T$

$$\Delta E = \frac{3}{2} \times 8.314 \times 100 = 1247.1 \text{ J} = 1.247 \text{ kJ}$$

Since the volume remains constant, $w = 0$

2. The amount of ice (in grams) that remains when 52 g of ice is added to 100 g of water at 40°C is ___.

Solution

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(2)

3. Standard Gibbs energy change for a reaction is zero. The value of equilibrium constant is ___.
Solution
(1) $K = e^{-\Delta G°/RT} = e^0 = 1$

4. When 100 mL of each of HCl and NaOH solutions are mixed, 5.71 kJ of heat was evolved. The molarity of the solutions is ___.
Solution
(1) Enthalpy of neutralization of a strong acid and a strong base is –57.54 kJ. It is the heat evolved when one gram equivalent of strong acid (HCl) is mixed with strong base (NaOH). Since 100 ml of 1 g-equiv solution evolves 5.71 kJ of heat, so the molarity of the solution is 1.
5. Enthalpy of neutralization of HCl by NaOH is –57.32 kJ mol^{-1} and by NH_4OH is –51.34 kJ mol^{-1}. Calculate the enthalpy of dissociation of NH_4OH.
Solution
(6) Given that
$H^+(aq) + NH_4OH\ (aq) \rightarrow NH_4^+(aq) + H_2O(l)$ $\Delta_r H$ = –51.34 kJ mol^{-1}
We may consider neutralization in two steps:
(i) Ionization: $NH_4OH(aq) \rightarrow NH_4^+(aq) + OH^-\ (aq)$; $\Delta_r H_1$?
(ii) Neutralization: $H^+(aq) + OH^-\ (aq) \rightarrow H_2O(l)$; $\Delta_r H_2$ = –57.32 kJ mol^{-1}
Now, $\Delta_r H = \Delta_r H_1 + \Delta_r H_2$
Therefore, $\Delta_r H_1 = \Delta_r H + \Delta_r H_2$ = –51.34 4 – 57.32 = 5.98 kJ $mol^{-1} \cong 6$
6. A gas expands against a constant external pressure so that the work done is 607.8 J. The work done in liter atmosphere is ___.
Solution
(6) 1 atm L = 101.325 J. Therefore, 607.8 J = $\frac{1}{101.325} \times 607.8 = 5.99 \cong 6$ L atm.

7. For the equilibrium reaction, the value of Gibbs energy is ___.
Solution
(0) $\Delta G = 0$ at equilibrium.

Matrix Match Type
1. Match the process with the expression.

Column I	**Column II**
(A) For spontaneous	(p) $\sum \Delta_{bond} H(\text{reactants}) - \sum \Delta_{bond} H(\text{products})$
(B) For endothermic	(q) $\Delta_r H = \Delta_r U$
(C) Bond dissociation energy	(r) $\Delta G < 0$
(D) For solids and liquids in a thermochemical reaction	(s) $\sum H(\text{products}) > \sum H(\text{reactants})$

Solution
A → (r); B → (s); C→ (p); D→ (q).
(A) Gibbs free energy is negative for spontaneous process
(B) Heat is absorbed in case of endothermic process
(C) Bond dissociation enthalpy is the energy needed to break 1 mol of the bond.
(D) $\Delta_r H = \Delta_r U + \Delta nRT$. Now, $\Delta n = 0$ for solids and liquids, so $\Delta_r H = \Delta_r U$.

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2. Match the gas with the ratio $\gamma = C_p/C_V$.

Column I	**Column II**
(A) Ammonia	(p) 1.20
(B) Carbon dioxide	(q) 1.30
(C) Carbon monoxide	(r) 1.40
(D) Helium	(s) 1.66

Solution

A → (s), B → (r), C → (q), D → (p)

3. Match the process with the correct expressions

Column I	**Column II**
(A) Isochoric process	(p) ΔS
(B) Isobaric process	(q) $\Delta q = 0$ as $\Delta U = q + w$
(C) Isothermal process	(r) $w = 0$
(D) Adiabatic process	(s) $\Delta T = 0$

Solution

A → (r); B → (s); C→ (p, s); D → (q, s)

4. Match the signs of ΔH and ΔS with the nature of the reaction.

Column I	**Column II**
(A) Negative and negative	(p) Spontaneous only at low temperature.
(B) Negative and positive	(q) Spontaneous only at high temperature.
(C) Positive and positive	(r) Spontaneous at all temperature.
(D) Positive and negative	(s) Non-spontaneous at all temperature.

Solution

A → (p), B → (r), C → (q), D → (s)

Using the equation $\Delta G = \Delta H - T\Delta S$

5. Match the column correctly:

Column I	**Column II**
(A) Extensive properties	(p) Density (at constant p, V, and T)
(B) Closed system	(q) Bursting of tire
(C) Path function	(r) Additive in nature
(D) Adiabatic	(s) U □ constant
(E) Intensive properties	(t) Heat

Solution

A → (r); B → (t); C → (s); D → (q); E → (p)

(A) Extensive properties depend on the quantity of matter present in the system.

(B) If the system exchanges only energy with the surroundings and not the matter.

(C) Path functions are those that depend only on the path and not the state of the system.

(D) In adiabatic process, no heat can flow from the system to the surroundings and vice versa.

(E) Intensive properties are those that do not depend on the matter present in the system.

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