

#420101

Topic: Different types of heats/enthalpies of reaction

Given below are observations on molar specific heats at room temperature of some common gases

Gas	Molar specific heat (C_v)($\text{cal mol}^{-1} \text{K}^{-1}$)
Hydrogen	4.87
Nitrogen	4.97
Oxygen	5.02
Nitric oxide	4.99
Carbon monoxide	5.01
Chlorine	6.17

The measured molar specific heats of these gases are markedly different from those for monatomic gases. Typically molar specific heat of a monatomic gas is 2.92 cal/mol K . Explain this difference. What can you infer from the somewhat larger (than the rest) value for chlorine?

Solution

The gases listed in the given table are diatomic. Besides the translational degree of freedom, they have other degrees of freedom (modes of motion).

Heat must be supplied to increase the temperature of these gases. This increases the average energy of all the modes of motion. Hence, the molar specific heat of diatomic gases is more than that of monatomic gases.

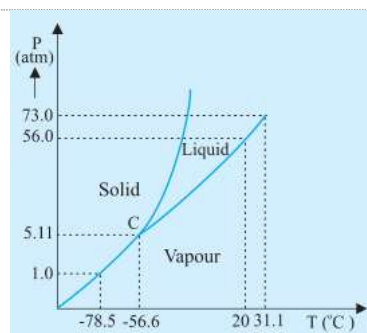
If only rotational mode of motion is considered, then the molar specific heat of a diatomic gas = $(5/2) R$

$$= (5/2) \times 1.98 = 4.95 \text{ cal/ mol.K}$$

With the exception of chlorine, all the observations in the given table agree with $(5/2)R$.

This is because at room temperature, chlorine also has vibrational modes of motion besides rotational and translational modes of motion.

#420150

Topic: Some basic terms and concepts

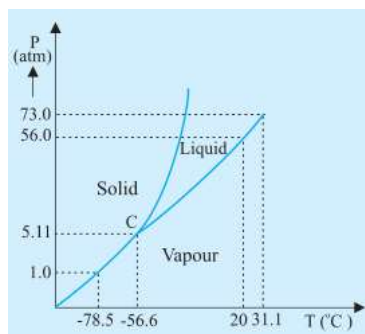
Answer the following questions based on the P-T phase diagram of carbon dioxide:

- At what temperature and pressure can the solid, liquid and vapour phases of CO_2 co-exist in equilibrium?
- What is the effect of decrease of pressure on the fusion and boiling point of CO_2 ?
- What are the critical temperature and pressure for CO_2 ? what is their significance?
- Is CO_2 solid, liquid or gas at (a) -70°C under 1 atm, (b) -60°C under 10 atm, (c) 15°C under 56 atm?

Solution

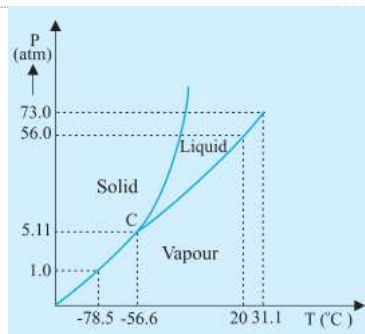
The P-T phase diagram for CO_2 is shown in the attached figure.

- (a) The three phases can coexist at triple point. From the graph, it is at -56.6°C and 5.11 atm.
- (b) With the decrease in pressure, both the fusion and boiling point of carbon dioxide will decrease.
- (c) For carbon dioxide, the critical temperature is 31.1°C and critical pressure is 73.0 atm. If the temperature of carbon dioxide is more than 31.1°C , it can not be liquefied, however large pressure we may apply.
- (d) Carbon dioxide will be (a) a vapour, at $= 70^\circ\text{C}$ under 1 atm. (b) a solid, at -6°C under 10 atm (c) a liquid, at 15°C under 56 atm.



#420195

Topic: Some basic terms and concepts



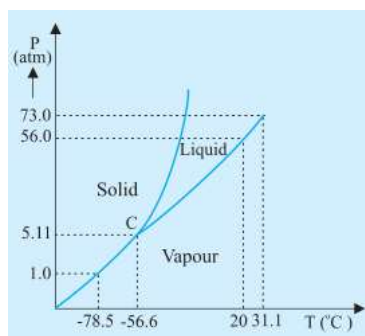
Answer the following questions based on the P-T phase diagram of CO_2 .

- (a) CO_2 at 1 atm pressure and temperature -60°C is compressed isothermally. Does it go through a liquid phase?
- (b) What happens when CO_2 at 4 atm pressure is cooled from room temperature at constant pressure?
- (c) Describe qualitatively the changes in a given mass of solid CO_2 at 10 atm pressure and temperature -65°C as it is heated up to room temperature at constant pressure.
- (d) CO_2 is heated to a temperature 70°C and compressed isothermally. What changes in its properties do you expect to observe?

Solution

The P-T phase diagram for CO_2 is shown in the following figure:

- (a) Since the temperature -60°C lies to the left of -56.6°C on the curve i.e. lies in the region vapour and solid phase, so carbon dioxide will condense directly into the solid without becoming liquid.
- (b) Since the pressure 4 atm is less than 5.11 atm the carbon dioxide will condense directly into solid without becoming liquid.
- (c) When a solid CO_2 at 10 atm pressure and -65°C temperature is heated, it is first converted into liquid. A further increase in temperature brings it into the vapour phase. At 10 atm, if a horizontal line is drawn parallel to the T-axis, then the points of intersection of this line with the fusion and vaporization curve will give the fusion and boiling points of CO_2 at 10 atm.
- (d) Since 70°C is higher than the critical temperature of CO_2 , so the CO_2 gas can not be converted into liquid state on being compressed isothermally at 70°C . It will remain in the vapour state. However, the gas will depart more and more from its perfect gas behavior with the increase in pressure.



#422981

Topic: Some basic terms and concepts

Choose the correct answer.

A thermodynamic state function is a quantity :

- ☐ A used to determine heat changes
- ☒ B whose value is independent of path
- ☐ C used to determine pressure volume work
- ☐ D whose value depends on temperature only

Solution

A thermodynamic state function is a quantity whose value is independent of path. Thus, enthalpy is a state function.

Its value depends on initial and final states and is independent of path followed.

#422982

Topic: Some basic terms and concepts

For the process to occur under adiabatic conditions, the correct condition is :

- ☐ A $\Delta T = 0$
- ☐ B $\Delta p = 0$
- ☒ C $q = 0$
- ☐ D $w = 0$

Solution

For the process to occur under adiabatic conditions the correct condition is $q=0$.

There is no exchange of heat.

#422983

Topic: Different types of heats/enthalpies of reaction

The enthalpies of all elements in their standard states are :

- ☐ A unity
- ☒ B zero
- ☐ C < 0
- ☐ D different for each element

Solution

The enthalpies of all elements in their standard states are zero.

Thus, the enthalpies of Na(s), K(s) He(g) etc. in their standard states are zero.

#422986

Topic: Measurement of delta U and delta H - Calorimetry

ΔU° of combustion of methane is $-X \text{ kJ mol}^{-1}$. The value of ΔH° is:

- ☐ A $=\Delta U^\circ$
- ☐ B $>\Delta U^\circ$
- ☒ C $<\Delta U^\circ$
- ☐ D $= 0$

Solution

ΔU° of combustion of methane is $-X \text{ kJ mol}^{-1}$. The value of ΔH° is $< \Delta U^\circ$

For the combustion of methane, Δn is negative.

Hence, $\Delta H^\circ = \Delta U^\circ + \Delta nRT < \Delta U^\circ$

#422991

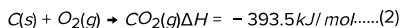
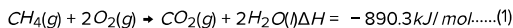
Topic: Different types of heats/enthalpies of reaction

The enthalpy of combustion of methane graphite and dihydrogen at 298K are $-890.3 \text{ kJ mol}^{-1}$ and $-285.8 \text{ kJ mol}^{-1}$ respectively. Enthalpy of formation of $\text{CH}_4(\text{g})$ will be :

- ☒ A $-78.8 \text{ kJ mol}^{-1}$
- ☐ B $-52.27 \text{ kJ mol}^{-1}$
- ☐ C $+74.8 \text{ kJ mol}^{-1}$
- ☐ D $+52.26 \text{ kJ mol}^{-1}$

Solution

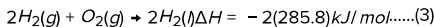
The combustion reactions are shown below.



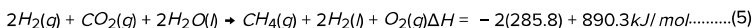
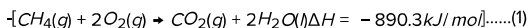
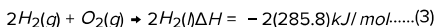
The equation for the formation of methane is



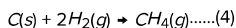
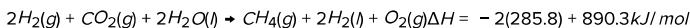
Multiply equation 3 with 2



Subtract equation 1 from equation (3)



add equation 2 to equation (5) to form equation 4.



$$\Delta H = -393.5 + 2(-285.8) - (-890.3) = -74.8 \text{ kJ/mol}$$

#422993

Topic: Entropy and gibbs free energy

A reaction $A+B \rightarrow C+D$ is found to have a positive entropy change. The reaction will be :

- ☐ A possible at high temperature
- ☐ B possible only at low temperature
- ☐ C not possible at any temperature
- ☒ D possible at any temperature

Solution

A reaction $A + B \rightarrow C + D$, is found to have a positive entropy change.

The reaction will be possible at any temperature.

A spontaneous reactions proceed with increase in entropy.

A non spontaneous reaction proceeds with decrease in entropy.

#422995

Topic: First law of thermodynamics

In a process 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process ?

Solution

System absorbs 701 J of heat which has positive sign and does 394 J of work which has negative sign.

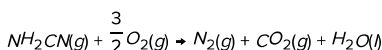
According to the first law of thermodynamics,

$$\Delta U = q + w = 701 - 394 = 307 \text{ J}$$

#423003

Topic: Measurement of delta U and delta H - Calorimetry

The reaction of cyanamide $NH_2CN(g)$ with dioxygen was carried out in a bomb calorimeter and ΔU was found to be $-742.7 \text{ kJ mol}^{-1}$ at 298 K. Calculate enthalpy change for the reaction at 298 K.



Solution

For given reaction, $\Delta n = 1 + 1 - 1.5 = 0.5$.

$$\Delta H = \Delta U + \Delta n_g RT$$

$$= -742.7 + 0.5 \times 8.314 \times 10^{-3} \times 292 = -742.7 + 1.2 = -741.5 \text{ kJ mol}^{-1}$$

#423047

Topic: Heat capacity, specific heat capacity and molar heat capacity

Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to ice at -10.0°C

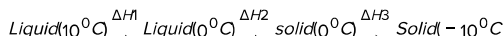
$$\Delta_{\text{fus}}H = 6.03 \text{ kJ mol}^{-1} \text{ at } 0^\circ\text{C}$$

$$C_p[H_2O(l)] = 75.3 \text{ J mol}^{-1}\text{K}^{-1}$$

$$C_p[H_2O(s)] = 36.8 \text{ J mol}^{-1}\text{K}^{-1}$$

Solution

The process is represented below.



$$\Delta H_1 = n C_p[H_2O(l)] \times \Delta T = 1 \times 75.3 \times 10 = 753 \text{ J/mol} = 0.753 \text{ kJ/mol}$$

$$\Delta H_2 = n(-\Delta_{\text{fus}}H^\circ) = -1 \times 6.03 = -6.03 \text{ kJ/mol}$$

$$\Delta H_3 = n C_p[H_2O(s)] \times \Delta T = 1 \times 36.8 \times 10 = 368 \text{ J/mol} = 0.368 \text{ kJ/mol}$$

$$\Delta H_1 + \Delta H_2 + \Delta H_3 = 0.753 - 6.03 - 0.368 = -5.645 \text{ kJ/mol}$$

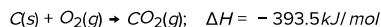
#423053

Topic: Different types of heats/enthalpies of reaction

Enthalpy of combustion of carbon to CO_2 is $-393.5 \text{ kJ mol}^{-1}$. Calculate the heat released upon formation of 35.2g of CO_2 from carbon and dioxygen gas.

Solution

The balanced chemical reaction for the combustion of C to CO_2 is given below.



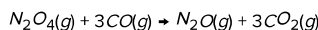
The formation of 4 g (1 mol) of CO_2 releases 393.5 kJ of heat.

The formation of 35.2 g of CO_2 releases $\frac{393.5 \times 35.2}{44} = 314.8 \text{ kJ}$ of heat.

#423056

Topic: Different types of heats/enthalpies of reaction

Enthalpies of formation of $\text{CO}(g)$, $\text{CO}_2(g)$, $\text{N}_2\text{O}(g)$ and $\text{N}_2\text{O}_4(g)$ are -110 , -393.81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction.

**Solution**

The balanced chemical reaction is $\text{N}_2\text{O}_4(g) + 3\text{CO}(g) \rightarrow \text{N}_2\text{O}(g) + 3\text{CO}_2(g)$



The enthalpy change for the reaction is $\Delta_r H = \Delta_f H[\text{N}_2\text{O}(g)] + 3\Delta_f H[\text{CO}_2(g)] - [\Delta_f H[\text{N}_2\text{O}_4(g)] + 3\Delta_f H[\text{CO}(g)]]$

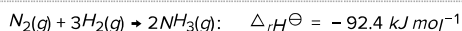
$$\Delta_r H = 81 + 3(-393) - [9.7 + 3(-110)]$$

$$\Delta_r H = -777.7 \text{ kJ/mol}$$

Hence, the enthalpy change for the reaction is -777.7 kJ/mol .

#423064

Topic: Different types of heats/enthalpies of reaction



What is the standard enthalpy of formation of NH_3 gas?

Solution

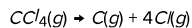
When 1 mole of ammonia is formed from its elements, the enthalpy change is known as the enthalpy of formation. It is equal to one half the value of the enthalpy change associated with formation of 2 moles of ammonia.

Hence, the enthalpy of formation of ammonia is $\frac{92.4}{2} = -46.1 \text{ kJ/mol}$.

#423087

Topic: Different types of heats/enthalpies of reaction

Calculate the enthalpy change for the process

and calculate bond enthalpy of C-Cl in $CCl_4(g)$

$$\Delta_{vap}H^\ominus(CCl_4) = 30.5 \text{ KJ mol}^{-1}$$

$$\Delta_f H^\ominus(CCl_4) = -135.5 \text{ KJ mol}^{-1}$$

$$\Delta_a H^\ominus(C) = 715.0 \text{ KJ mol}^{-1} \text{ where } \Delta_a H^\ominus \text{ is enthalpy of atomisation}$$

$$\Delta_a H^\ominus(Cl_2) = 242 \text{ KJ mol}^{-1}$$

Solution

$$\Delta_f H^\ominus(CCl_4)(g) = 30.5 - 135.5 = -105.0 \text{ kJ/mol}$$

For the given process

$$\Delta H^\ominus = \Delta_a H^\ominus(C) + 4\Delta_a H^\ominus(Cl) - \Delta_f H^\ominus(CCl_4)(g) = 715.0 + 2 \times 242 - (-105.0) = 1304.0 \text{ kJ/mol}$$

#423088

Topic: Some basic terms and conceptsFor an isolated system $\Delta U=0$ what will be ΔS ?**Solution**

Consider an isolated system of two gases present in two separate containers joined by a stopcock. Since the system is isolated from surroundings, $\Delta U = 0$. When the stop cock is opened, two gases mix up and the system becomes more disordered.

Hence, $\Delta S > 0$

#423089

Topic: Heat capacity, specific heat capacity and molar heat capacity

For the reaction at 298 K



$$\Delta H = 400 \text{ KJ mol}^{-1} \text{ and } \Delta S = 0.02 \text{ KJ K}^{-1} \text{ mol}^{-1}$$

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range**Solution**

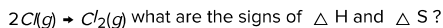
$$\Delta G = \Delta H - T\Delta S = 0$$

$$T = \frac{\Delta H}{\Delta S} = \frac{400}{0.2} = 2000 \text{ K}$$

#423090

Topic: Entropy and gibbs free energy

For the reaction

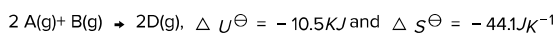
**Solution**

ΔH is negative (bond energy is released and the reaction is exothermic) and ΔS is negative (There is less randomness among the molecules than among the atoms). In other words, the number of moles of gaseous species decreases during the reaction.

#423092

Topic: Entropy and gibbs free energy

For the reaction

Calculate ΔG^\ominus for the reaction and predict whether the reaction may occur spontaneously**Solution**

The change in the number of moles of gaseous species is

$$2 - 3 = -1$$

$$\Delta H^\ominus = \Delta U^\ominus + \Delta n_g RT = -10.5 + (-1) \times 8.314 \times 10^{-3} \times 298 = -12.98 \text{ kJ}$$

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus = -12.98 - 298(-44.1 \times 10^{-3}) = 0.16 \text{ kJ}$$

#423095

Topic: Entropy and gibbs free energy

The equilibrium constant for a reaction is 10. what will be value of ΔG^\ominus ? $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 300 \text{ K}$

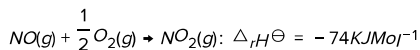
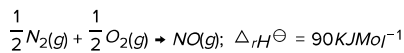
Solution

$$\Delta G^\ominus = -2.303RT \log K = -2.303 \times 8.314 \times 300 \log 10 = -5.744 \text{ kJ/mol}$$

#423097

Topic: Different types of heats/enthalpies of reaction

Comment on the thermodynamic stability of NO(g) given

**Solution**

The enthalpy of formation of NO has positive value. Hence, NO is unstable. During formation of NO_2 , energy is released. Hence, NO_2 is formed.

#423263

Topic: Entropy and gibbs free energy

Calculate a) ΔG^\ominus b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298

**Solution**

$$(a) \Delta G^\ominus = \Delta_f G^\ominus(\text{NO}_2) - [\Delta_f G^\ominus(\text{NO}) + 1/2 \Delta_f G^\ominus(\text{O}_2)] = 52.0 - 87.0 - 1/2 \times 0 = -35 \text{ kJ/mol}$$

$$(b) \log K = \frac{-\Delta G^\ominus}{2.303RT} = -\frac{-35 \times 10^3}{2.303 \times 8.314 \times 298} = 6.314$$

$$K = 1.362 \times 10^6$$

#423960

Topic: Different types of heats/enthalpies of reaction

Calculate the entropy change in surrounding when 1.00 mol of $\text{H}_2\text{O}(\text{l})$ is formed under standard condition $\Delta_f H^\ominus = -286 \text{ kJ mol}^{-1}$

Solution

Formation of water under standard conditions is an exothermic process. During the process heat is given out by the system to surrounding. Hence,

$$q_{\text{surr}} = +286 \text{ kJ/mol}$$

$$\text{The expression for the entropy change is } \Delta S = \frac{q}{T}$$

Substitute values in the above expression.

$$\Delta S = \frac{286 \times 1000}{298} = 959 \text{ J/K/mol}$$