

## Thermodynamics

An alert young student with little background in chemistry might be surprised that a subject named "thermodynamics" has any relevance to chemical change, or to biological and geological systems. The term thermodynamics literally connotes a scientific discipline concerned with mechanical action produced by heat. Indeed the origin of thermodynamics lies in the analysis by Carnot, in 1824, of the performance of heat engines. His famous book on this subject in fact bears the title *Reflections on the Motive Power of Heat*.

In the course of the analysis of the mechanical efficiency of steam engines, by Carnot and by other great physicists of the middle nineteenth century (Joule, Mayer, Kelvin, Clausius, Helmholtz), two principles emerged, now called the first and second laws of thermodynamics. In time it also became apparent that these principles have significance far beyond engineering problems and, in fact, govern all transformations of energy, including transformations in chemical, biological, and geological systems in which an accompanying energy change may not even be evident. The great universality of the two laws of classical thermodynamics is so impressive that Einstein was prompted to make the following comment:

A theory is the more impressive the greater is the simplicity of its premises, the more different are the kinds of things it relates and the more extended is its range of applicability. Therefore, the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced, that within the framework of applicability of its basic concepts, will never be overthrown.

What then are these two great principles or fundamental concepts of thermodynamics?

The first is the concept of energy and the associated principle of conservation of energy. Historically the concept of energy arose first in the analysis of purely mechanical phenomena. It was recognized early in mechanics that if work were done to lift a weight in air from one vertical position in a gravitational field to another, this work could be fully recovered (ignoring trivial losses due to friction); that is, the lifted weight, if suitably connected, could lift another object. Thus one may assign to the weight in the top vertical position a certain "capacity to do work" which is inherent in the weight by virtue of its position in the gravitational field. This capacity to do work depends only on the height of the weight above some reference point (e.g., sea level). It seemed appropriate, therefore, to assign a special name, energy, to this capacity to do work, and perhaps to add an adjective internal to energy to emphasize the inherent nature of this capability.

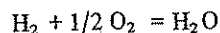
In contrast if a weight is moved horizontally across a rough floor from left to right, the weight in the final position at the right does not retain the capacity to regenerate the work done upon it. In fact one must do work on it to return the weight to its initial position. Clearly in this situation the exertion of work on a body does not result in giving it internal energy.

In parallel with historical development we recognize sooner or later an important distinction between these two situations. In the second, friction is dominant and heat is evolved as the weight is moved along the floor. Since no student approaches this subject without some background in physics, he will at this point immediately say that we could call heat a form of energy. We should recognize, first, however, that in doing so we have definitely departed from our initial definition that energy is the capacity to do work. Furthermore, there would be no advantage in making heat comparable to work unless the two were quantitatively interrelated. As every student knows, however, this quantitative equivalence has been demonstrated in the experiments of Joule.

To encompass situations involving heat as well as work we generalize our definition of energy to the statement

Change in internal energy of a system = heat absorbed by system + work done on the system

Using this definition of energy we find as a matter of universal experience that "energy is conserved." What this means is that the change in energy in going from one state to another is always the same even though the heats absorbed or works done may be different in each of several pathways of making this transition. For example in a battery, or fuel cell, in which the chemical reaction is

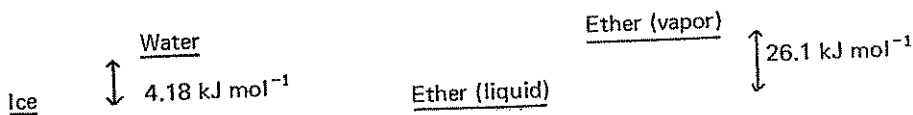


we can operate the battery in several different ways. (1) We could short-circuit it; in this case no work is done and much heat is evolved. (2) We could have it run an inefficient motor; in this case some work is done and less heat is evolved. (3) We could let it operate a highly efficient motor; in this case more work is done and even less heat is evolved. Nevertheless quantitative calculations show that in all three cases the net change in internal energy is identical. This is what we mean by conservation of energy.

Let us turn now to the second law of thermodynamics. The problem that this addresses itself to is the following. How can we tell beforehand whether a given chemical or physical transformation can occur spontaneously or cannot?

The first law of thermodynamics does not provide us with a criterion for determining this. One unfamiliar with energetics is accustomed to thinking that a chemical or physical change may occur spontaneously only if the final state of the system is at a lower level of energy than the initial, i.e., only if there is a drop in internal energy of the system. This conclusion is based on thoroughly valid common experience with movements in gravitational fields. We all recognize that a ball tends to fall from a higher to a lower level, not vice versa. For purely mechanical processes, involving no heat exchange, the rule that there must be a drop in energy is valid as a criterion of permissible spontaneous change. What is not often realized is that this rule is completely unreliable if applied to all kinds of transformations.

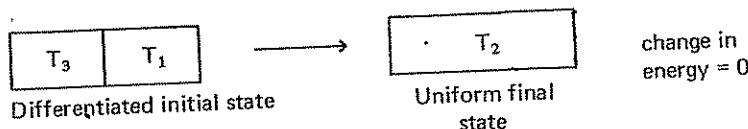
There are spontaneous transformations that occur despite the fact that the internal energy of the system at the end is essentially the same as before the transformation. For example, when a stretched rubber band is released, it snaps back spontaneously; yet the internal energy change for this process is substantially zero. Similarly when an ideal gas restrained by a piston with a heavy weight is freed from that pressure and restrained by a lower external pressure the gas will expand spontaneously; yet the internal energy change for this process is also zero. When a hot block of metal is placed next to a cold one (in an insulated container) heat will flow spontaneously from the hot to cold material; yet the change in internal energy is zero. There are even processes that can occur spontaneously despite the fact that the internal energy at the end is greater than at the beginning of the transformation. Two examples are shown below:



Thus, liquid water has a higher internal energy than ice. Nevertheless, if ice were at 1 °C it would change spontaneously to water, it would spontaneously increase its internal energy and go "uphill." Liquid ether behaves similarly in going spontaneously (at 35 °C) to gaseous ether. Neither violates conservation of energy in doing so, for each would absorb the needed energy from the air around it.

Thus we see that change in internal energy is no basis for deciding whether a transformation can occur spontaneously. Some further principle is required to summarize in a general statement the observed tendency of systems of many different types to change in a particular direction.

Let us reexamine some of the examples of spontaneous transformations just mentioned. If we have two blocks of metal at a higher temperature  $T_3$  and a lower temperature  $T_1$ , respectively,



the system will tend to go spontaneously to a final state of uniform intermediate temperature. In the original state the system could do work; for example we could put one thermocouple in  $T_3$  and another in  $T_1$  and obtain electrical work. In the final state the capacity to do work has been lost.

Similarly if we have a stretched rubber band or spring



the system will spontaneously collapse. Again in the initial state we could obtain work by a suitable mechanical coupling of the rubber band to a pulley, for example. In the final state the capacity to do work has been lost.

In these examples as well as in the myriad of other unidirectional spontaneous transformations examined, Kelvin and Clausius first recognized that even though the change in energy might be zero, the ability to use internal energy for work has been lost when we reach the final state. The system thus has become more "exhausted." A careful analysis shows that it is even possible to derive a quantitative measure of this "exhaustion," an "index of exhaustion." This "index" has been called the entropy. The higher the entropy, the greater the exhaustion, the greater the loss in ability to use internal energy for work.

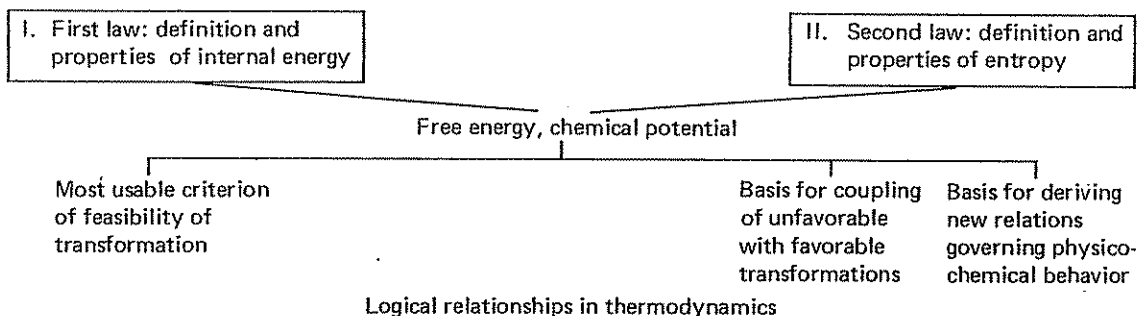
Spontaneous transformations occur all around us all the time. Very general observations of the world around us show that all observable spontaneous changes go in the direction which decreases the capacity for

further spontaneous change, and that the universe (or at least the solar system) changes in time toward a state in which (ultimately) no further spontaneous change will be possible. We need merely cite again a few examples: solutes always diffuse from a more concentrated solution to a dilute one; clocks tend to run down; magnets become self-demagnetized; heat always flows from a warm body to a colder one; gases always effuse into a vacuum; aqueous solutions of NaCl and AgNO<sub>3</sub> if mixed always form AgCl. Although some of these individual changes can be reversed by some outside agency, this outside agent must itself undergo a transformation which decreases its capacity for further spontaneous change. It is impossible to restore every system back to its original condition. On earth, our ultimate source of energy for work is the sun or nuclear power; in either case, these ultimate nuclear reactions proceed unidirectionally and toward the loss of capacity for further spontaneous change. Thus, the "index of exhaustion," the entropy, is always getting larger and larger. This realization led Clausius to his famous aphorism:

The energy of the universe is constant; the entropy strives toward a maximum.

The first part of this saying is the first law of thermodynamics; the second part is a concise phrasing of the second law.

During the second half of the nineteenth century the scope of applications of thermodynamics was extensively widened. This development was greatly facilitated by a fusion of the first and second laws into a single quantity, the "free energy" or "chemical potential."

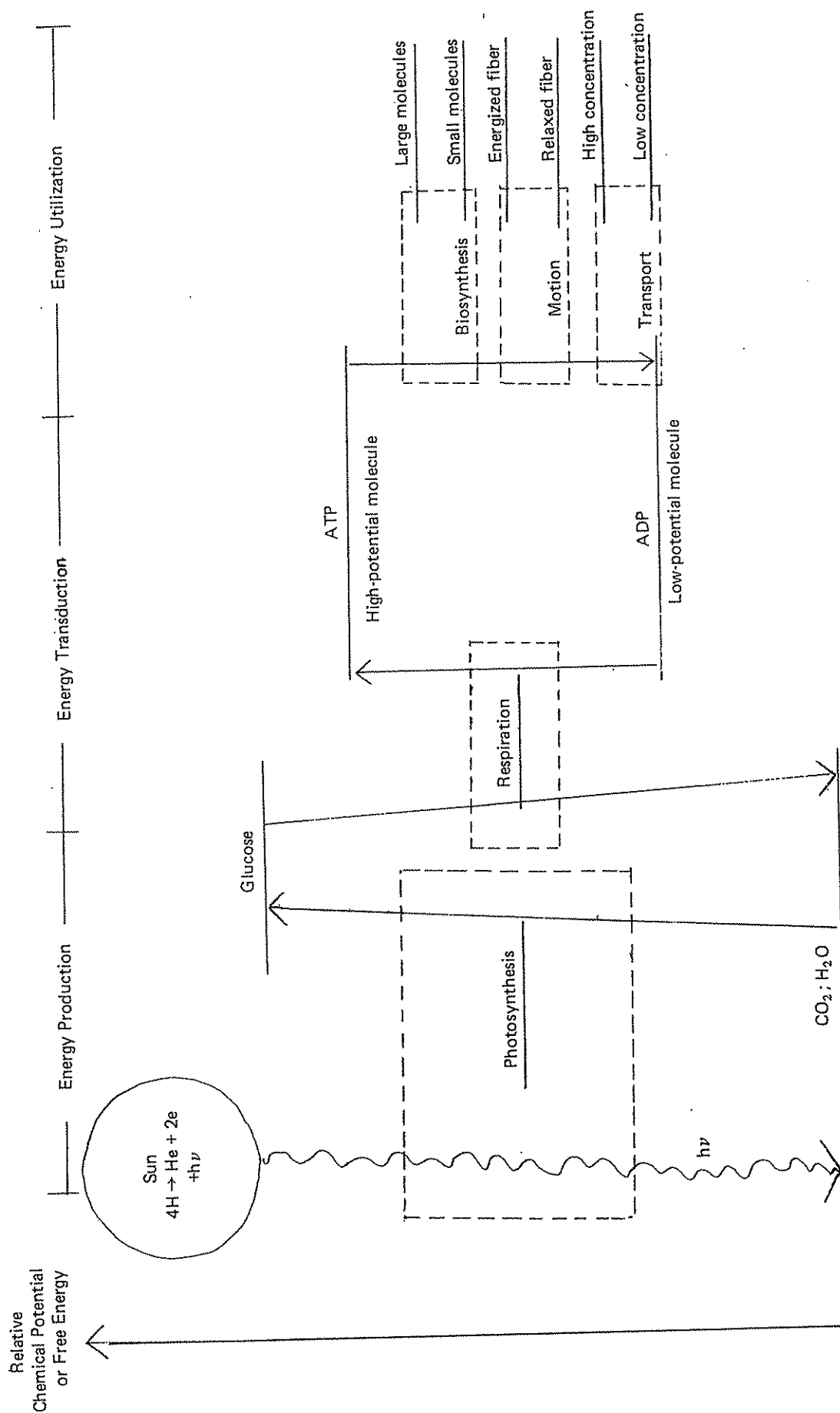


The most influential contributor in this direction was J. Willard Gibbs, the greatest of native-born American scientists. He formulated the principles of thermodynamics in a very sophisticated and powerful mathematical format out of which has come a wealth of new conceptual and experimental interrelationships. These have been immensely fruitful in extending thermodynamic reasoning from physics and engineering to chemistry, biology, and geology. For example, thermodynamic principles permit the computation of the maximum yield in the synthesis of ammonia from nitrogen and hydrogen under a variety of conditions of temperature and pressure, with important consequences to the chemical fertilizer industry. Similarly, the equilibrium distribution of sodium and potassium ions between red blood cells and blood plasma can be calculated from thermodynamic relationships. The observation of deviations from an equilibrium distribution led to a search for mechanisms of active transport of the alkali metal ions across the cell membrane. Thermodynamic calculations of the effect of temperature and pressure on the transformation between graphite and diamond generate hypotheses about the geological conditions under which natural diamonds were produced, as well as predictions of the conditions under which synthetic diamonds can be made.

One of the currently very active and exciting areas of application of thermodynamics is to energy flow in the living world. A schematic outline of this flow is illustrated below. The ultimate source of all energy used by living organisms is the sun. In photosynthesis, green plants and microorganisms convert carbon dioxide and water to glucose and thereby transform light energy to chemical energy. However, the chemical potential or free energy in glucose is not used directly to operate the essential functions of the cell (e.g., biosynthesis, motion, concentrating substances across membranes, etc.), probably because the amount stored in each glucose molecule is in too large a packet (about 2900 kJ mol<sup>-1</sup>). Rather, the chemical potential in glucose is "transduced" or divided up into smaller packets (of about 42 kJ mol<sup>-1</sup>) and stored in special "energy-distributing intermediates" by means of the many interlinked chemical reactions that occur in cellular respiration. The distributor molecules then give up their chemical potential or free energy, in a variety of different ways, to operate the essential functions of a living cell and organism. Elucidation of the specific chemical transformations involved is essential to an understanding of the flow of energy in the living world. Insights into all of these transformations are being obtained by application of thermodynamic concepts and principles.

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# ENERGY FLOW IN LIVING WORLD



- S-1 Heat is that form of energy which passes from one body to another as the result of a temperature difference between the two bodies. The amount of energy transferred is expressed in the unit of joules.

$$1 \text{ joule (J)} = 1 \text{ newton meter (N m)}$$

$$1 \text{ joule} = 0.239 \text{ calories}$$

		Q-1	Why does a block of ice feel cold to your touch?
A-1	When your finger touches the block of ice which is at a lower temperature, heat is transferred from your finger to the block of ice. The loss in heat from your finger makes the block of ice feel cold.	Q-2	According to the kinetic molecular theory, in order to boil a substance the molecules must obtain enough energy to overcome the forces of attraction between neighboring molecules. Describe how this energy is obtained when a substance such as water is boiled over a campfire.
A-2	A flame is placed under a container of water, and energy is transferred from the hot flame to the cool water. This heat increases the kinetic energy of the water molecules.	Q-3	The specific heat of a substance is defined as the amount of heat necessary to raise one gram of the substance one degree kelvin ( $\text{J g}^{-1} \text{K}^{-1}$ ). A 10 g sample of $\text{H}_2\text{O}$ absorbs 251 joules of heat.  The temperature rises from $10^\circ\text{C}$ to $16^\circ\text{C}$ . What is the specific heat of water?
A-3	$\frac{251 \text{ J}}{10 \text{ g} \cdot 6 \text{ K}} = 4.18 \text{ J g}^{-1} \text{K}^{-1}$	Q-4	How much heat in joules is necessary to raise the temperature of 25 grams of $\text{H}_2\text{O}$ $25^\circ\text{C}$ ?
A-4	$\frac{25 \text{ g H}_2\text{O} \cdot 4.18 \text{ J}}{\text{g K}} \cdot 25 \text{ K} = 2.6 \times 10^3 \text{ J}$	Q-5	A quantity of 200 g of $\text{H}_2\text{O}$ at $20^\circ\text{C}$ absorbs 50 kJ of heat.  What is the final temperature of the water?  1 kilojoule (kJ) = 1000 joules
A-5	Increase in temp = $\frac{50 \text{ kJ}}{1 \text{ kJ}} \cdot \frac{1000 \text{ J}}{4.18 \text{ J}} \cdot \frac{1 \text{ g K}}{200 \text{ g}} = 60 \text{ K}$  Final temperature = $20^\circ\text{C} + 60^\circ\text{C} = 80^\circ\text{C}$ .	Q-6	If the specific heat of a substance is $3.66 \text{ J g}^{-1} \text{K}^{-1}$ , how much heat is necessary to raise 500 g of the material from a temperature of $20.0^\circ\text{C}$ to a temperature of $80.0^\circ\text{C}$ ? Express in kilojoules.
A-6	Change in temp = $80.0 - 20.0 = 60.0^\circ\text{C}$ $\frac{500 \text{ g} \cdot 3.66 \text{ J}}{\text{g K}} \cdot \frac{60.0 \text{ K}}{1000 \text{ J}} = 110 \text{ kJ}$	Q-7	What will be the final temperature of 1000 g of material at $25.0^\circ\text{C}$ after 29.3 kJ of heat is transferred away from it? The specific heat of the material is $5.00 \text{ J g}^{-1} \text{K}^{-1}$ .

A-7      Loss in temp =  $\frac{29.3 \text{ kJ}}{1 \text{ kJ}} \times \frac{1000 \text{ J}}{5.00 \text{ J}} \times \frac{1 \text{ K}}{1000 \text{ }^\circ\text{C}} = 6.4 \text{ K}$   
 $25.0^\circ\text{C} - 6.4^\circ\text{C} = 18.6^\circ\text{C}$

R

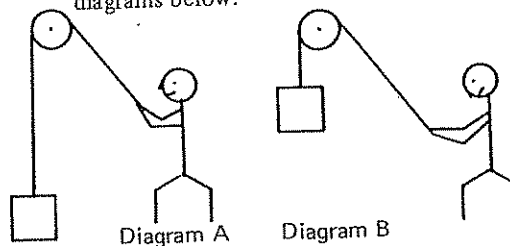
Heat is that form of energy which passes from one body to another as the result of a temperature difference between the two bodies.

Specific heat = amount of heat necessary to raise one gram of material one degree kelvin,  $\text{J g}^{-1} \text{K}^{-1}$ .

Specific heat of water =  $4.18 \text{ J g}^{-1} \text{K}^{-1}$

S-2      Another form of energy is work. The potential energy of a substance can be used to do work or, vice versa, work can be done to increase the potential energy of a substance. The Law of Conservation of Energy, introduced in Chapter 4 Part III, states that energy is neither created nor destroyed.

Q-8      Consider the system illustrated in the diagrams below.



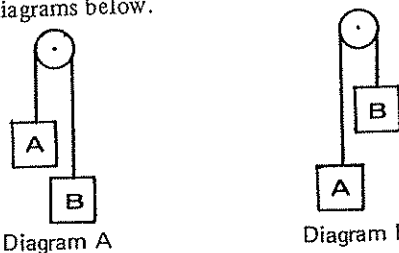
What happens to the potential energy of the block in going from diagram A to diagram B?

A-8      The potential energy increases due to an increase in height.

Q-9      Where did the energy come from in order for the block in Q-8 to increase its potential energy?

A-9      From the man. The energy is transferred by the man doing work by pulling the rope.

Q-10      Consider the system illustrated in the diagrams below.



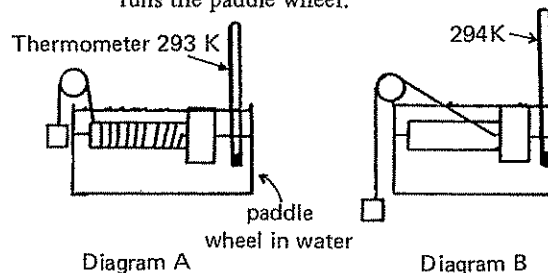
Weight A is 10 grams and weight B is 5 grams. What happens to the potential energy of weight A in going from diagram A to diagram B?

A-10 It decreases.

Q-11 In order to lift weight B as shown in Q-10 work must be performed. Where does the work come from?

A-11 Weight A. The potential energy lost by weight A can be used to do work.

Q-12 Consider the system illustrated in the diagrams below. The falling weight runs the paddle wheel.



What happens to the potential energy of the block in going from diagram A to diagram B?

A-12 The block loses potential energy.

Q-13 In the illustration of Q-12 the falling block supplied the energy to do the work necessary to turn the paddle wheel. What other form of energy is indicated in the diagrams?

A-13 The thermometer increased in temperature indicating that heat was supplied to the water.

Q-14 Where did the heat supplied to the water come from?

A-14 The work done by the paddle wheel was transferred into heat.

Q-15 According to the Law of Conservation of Energy if 1000 joules of work are done in increasing the potential energy of a block by 500 joules, what must happen to the rest of the energy in the process?

A-15 It must be transferred into heat.

R Work is another form of energy. The Law of Conservation of Energy states that the energy is neither created nor destroyed.

S-3 The Law of Conservation of Energy expressed in terms of the relationship between energy, heat, and work is called the First Law of Thermodynamics. This law is stated by the equation

$$\Delta E = Q + W$$

where  $\Delta E$  is the change in energy of a substance,  $Q$  is the heat absorbed by the substance, and  $W$  is the work done on the substance.

Q-16 For the example given in Q-15, how much heat must be given off in increasing the potential energy of the block the stated amount?

A-16  $\Delta E = Q + W$   
 $500 \text{ J} = Q + 1000 \text{ J}$   
 $-500 \text{ J}$  is the heat absorbed by the block;  
 therefore, it gave off  $+500 \text{ J}$  of heat.

This is the same as saying that half the energy supplied in raising the potential energy of the block went into supplying heat to the surroundings around the block.

Q-17 Consider a block falling from the table to the floor. If its potential energy decreases by  $2000 \text{ J}$ , how much work is done?

A-17 No work is done. The block falls freely to the floor.

Q-18 For the example in Q-17, what happens to the energy given up by the block?

A-18 It is given up to the floor in the form of heat when the block hits.

Q-19 How much heat is released to the floor in the process of Q-17?

A-19  $\Delta E = Q + W$   
 $\Delta E = -2000 \text{ J}$   
 $W = 0$   
 $Q = -2000 \text{ J}$   
 Therefore,  $2000 \text{ J}$  of heat is absorbed by the floor. (This assumes that the block itself doesn't change temperature.)

Q-20 In the example illustrated in Q-10 the energy of weight A changes by  $700 \text{ J}$ . The work done by the fall of A in lifting weight B is  $350 \text{ J}$ . How much heat is given off in the process? (Work done by an object is given a negative value.)

A-20  $\Delta E = Q + W$   
 $Q = \Delta E - W$   
 $W = \text{work done on weight A}$   
 $\Delta E = -700 \text{ J}$   
 $Q = -700 \text{ J} - (-350 \text{ J})$   
 $= -350 \text{ J}$   
 Heat given off =  $350 \text{ J}$

Q-21 If the energy change,  $\Delta E$ , for a chemical reaction is  $-50.0 \text{ kJ}$  and  $35.0 \text{ kJ}$  heat is given off by the reaction, how much work could be done by the reaction taking place?

A-21  $\Delta E = Q + W$   
 $\Delta E = -50.0 \text{ kJ}$   
 $Q = -35.0 \text{ kJ}$   
 $W = \Delta E - Q$   
 $= -50.0 \text{ kJ} + 35.0 \text{ kJ}$   
 $= -15.0 \text{ kJ}$   
 Work done by the reaction =  $15.0 \text{ kJ}$

R First Law of Thermodynamics

$$\Delta E = Q + W$$

where  $\Delta E$  is the change in energy of a substance,  $Q$  is the heat absorbed by the substance, and  $W$  is the work done on the substance.



- S-4 In a chemical reaction, heat is absorbed or released. For example, one mole of A can react with one mole of B to form one mole of C and give off 251 kJ of heat. This can be written in equation form as  $A + B \rightarrow C + 251 \text{ kJ}$ . This heat absorbed or released in a chemical reaction conducted at constant pressure is called the enthalpy change for the reaction,  $\Delta H$ . The  $\Delta$  refers to the difference in the sum of the enthalpies of the reactants and the products. The enthalpy change is expressed mathematically as

$$\Delta H = \sum_i n_i H_i (\text{products}) - \sum_i n_i H_i (\text{reactants})$$

where  $H_i$  and  $n_i$  are the enthalpy and moles, respectively, of the  $i^{\text{th}}$  substance.

For a process done at constant pressure and where no nonmechanical work is performed,

$$\Delta H = Q$$

Such processes would be typical of many chemical reactions carried out at atmospheric pressure.

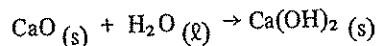
		Q-22	What is the enthalpy change ( $\Delta H$ ) for the chemical reaction $A \rightarrow B$ . $H$ for compound A is $209 \text{ kJ mol}^{-1}$ and $H$ for compound B is $418 \text{ kJ mol}^{-1}$ .
A-22	Conversion of one mole of A into one mole of B. $\Delta H = \sum nH (\text{products}) - \sum nH (\text{reactants})$ $\Delta H = (1 \text{ mol}) (418 \text{ kJ mol}^{-1}) - (1 \text{ mol}) (209 \text{ kJ mol}^{-1})$ $= 209 \text{ kJ}$	Q-23	The enthalpy of a substance can be considered as a measure of the amount of energy the substance contains. This is often referred to as heat content. Two substances A and B have heat contents of 100 and 140, respectively. Which substance has the greater energy? Why?
A-23	B. Since $H$ is a measure of the heat content, the substance with the larger heat content will have the greater energy.	Q-24	If in a chemical reaction, $A \rightarrow B$ , heat is given off, is the enthalpy of the product greater or less than that of the reactants? Why?
A-24	The enthalpy of the product must be lower because energy is released in going from the reactant to the product.	Q-25	A chemical reaction which gives off heat is called an <u>exothermic</u> reaction. What is the sign of $\Delta H$ for this type of reaction? Why?
Q-25	<u>Negative</u> . Since heat is given off in the reaction, the sum of the enthalpies of the products must be less than the sum of the enthalpies of the reactants. $\Delta H = \sum nH (\text{products}) - \sum nH (\text{reactants})$ In order for $\Delta H$ to be negative $\sum nH (\text{reactants}) > \sum nH (\text{products})$	Q-26	A chemical reaction which absorbs heat is called an <u>endothermic</u> reaction. Is the energy of the products greater or less than that of the reactants? Why?

- A-26 Greater. If heat is absorbed in the reaction,  
 $\Delta H = \sum nH_{\text{(products)}} - \sum nH_{\text{(reactants)}}$   
 In order for  $\Delta H$  to be positive  
 $\sum nH_{\text{(products)}} > \sum nH_{\text{(reactants)}}$

- Q-27 If the enthalpies of products and reactants are given in kilojoules for the reaction  $A + B \rightarrow C$ , the enthalpy change,  $\Delta H$ , for the conversion of one mole of A and one mole of B into one mole of C is  $-50 \text{ kJ}$ . What is  $\Delta H$  for the reaction if two moles of C are formed?

- A-27 If two moles of C are formed, the reaction would be  $2A + 2B \rightarrow 2C$ .  
 $\Delta H = 50 \text{ kJ mol}^{-1}$  of C formed.  
 For two moles,  
 $\Delta H = (2 \text{ mol}) \frac{(-50 \text{ kJ})}{\text{mol}}$   
 $= -100 \text{ kJ}$

- Q-28 What is the enthalpy change for the reaction



$$\begin{aligned} \text{if } H_{\text{CaO(s)}} &= -635.1 \text{ kJ mol}^{-1} \\ H_{\text{H}_2\text{O(l)}} &= -286.2 \text{ kJ mol}^{-1} \\ H_{\text{Ca(OH)}_2\text{(s)}} &= -984.9 \text{ kJ mol}^{-1} \end{aligned}$$

- A-28 For the conversion of one mole of CaO and one mole of  $\text{H}_2\text{O}$  into one mole of  $\text{Ca(OH)}_2$ ,

$$\Delta H = \sum nH_{\text{(p)}} - \sum nH_{\text{(r)}}$$

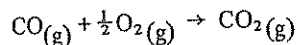
$$\Delta H = [(1 \text{ mol}) (-984.9 \text{ kJ mol}^{-1})] - [(1 \text{ mol}) (-286.2 \text{ kJ mol}^{-1}) + (1 \text{ mol}) (-635.1 \text{ kJ mol}^{-1})]$$

$$\Delta H = -63.6 \text{ kJ}$$

- Q-29 Is the reaction given in Q-28, exothermic or endothermic?

- A-29  $\Delta H = \text{negative value}$ . Therefore, the reaction is exothermic (gives off energy).

- Q-30 What is the enthalpy change for the reaction



$$\text{if } H_{\text{CO}} = -110.4 \text{ kJ mol}^{-1}$$

$$H_{\text{O}_2} = 0.0$$

$$H_{\text{CO}_2} = -393.3 \text{ kJ mol}^{-1} ?$$

Is the reaction endothermic or exothermic?

- A-30 For the conversion of one mole of CO and one half mole of  $\text{O}_2$  into one mole of  $\text{CO}_2$ ,

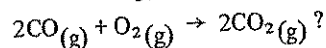
$$\Delta H = \sum nH_{\text{(p)}} - \sum nH_{\text{(r)}}$$

$$\Delta H = [(1 \text{ mol}) (-393.3 \text{ kJ mol}^{-1})] - [(0.0) + (1 \text{ mol}) (-110.4 \text{ kJ mol}^{-1})]$$

$$\Delta H = -282.9 \text{ kJ}$$

The reaction is exothermic.

- Q-31 What is the enthalpy change for the reaction



See Q-30 for enthalpies.

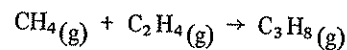
- A-31 For the conversion of two moles of CO and one mole of O<sub>2</sub> in two moles of CO<sub>2</sub>,

$$\Delta H = \sum nH_{(p)} - \sum nH_{(r)}$$

$$\Delta H = [(2 \text{ mol}) (-393.3 \text{ kJ mol}^{-1})] - [0.0 + (2 \text{ mol}) (-110.4 \text{ kJ mol}^{-1})]$$

$$\Delta H = -565.8 \text{ kJ}$$

- Q-32 What is the enthalpy change for the reaction



$$\text{if } H_{\text{CH}_4(\text{g})} = -74.9 \text{ kJ mol}^{-1}$$

$$H_{\text{C}_2\text{H}_4(\text{g})} = 52.3 \text{ kJ mol}^{-1}$$

$$H_{\text{C}_3\text{H}_8(\text{g})} = -103.8 \text{ kJ mol}^{-1}$$

Is the reaction exothermic or endothermic?

- A-32 For the conversion of one mole of CH<sub>4</sub> and one mole of C<sub>2</sub>H<sub>4</sub> into one mole of C<sub>3</sub>H<sub>8</sub>,

$$\Delta H = \sum nH_{(p)} - \sum nH_{(r)}$$

$$\Delta H = [(1 \text{ mol}) (-103.8 \text{ kJ mol}^{-1})] - [(1 \text{ mol}) (52.3 \text{ kJ mol}^{-1}) + (1 \text{ mol}) (-74.9 \text{ kJ mol}^{-1})]$$

$$\Delta H = -81.2 \text{ kJ}$$

The reaction is exothermic.

- Q-33 What is the enthalpy change for the reaction  $\text{C}_3\text{H}_8(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g}) + \text{CH}_4(\text{g})$ ?

Is the reaction exothermic or endothermic?

- A-33 For the conversion of one mole of C<sub>3</sub>H<sub>8</sub> into one mole of C<sub>2</sub>H<sub>4</sub> and one mole of CH<sub>4</sub>,

$$\Delta H = \sum nH_{(p)} - \sum nH_{(r)}$$

$$\Delta H = [(1 \text{ mol}) (52.3 \text{ kJ mol}^{-1}) + (1 \text{ mol}) (-74.9 \text{ kJ mol}^{-1})] - [(1 \text{ mol}) (-103.8 \text{ kJ mol}^{-1})]$$

$$\Delta H = 81.2 \text{ kJ}$$

Notice that  $\Delta H_{(\text{forward})} = -\Delta H_{(\text{reverse})}$  for any chemical reaction.

The reaction is endothermic.

- Q-34 What is the enthalpy change for the reaction  $\text{C}_2\text{H}_6\text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\ell) + \text{C}_2\text{H}_2(\text{g})$

$$\text{if } H_{\text{C}_2\text{H}_6\text{O}_2(\text{g})} = -528.4 \text{ kJ mol}^{-1}$$

$$H_{\text{H}_2\text{O}(\ell)} = -285.8 \text{ kJ mol}^{-1}$$

$$H_{\text{C}_2\text{H}_2(\text{g})} = 226.8 \text{ kJ mol}^{-1}?$$

Is the reaction exothermic or endothermic?

- A-34 For the conversion of one mole of  $\text{C}_2\text{H}_6\text{O}_2$  into two moles of  $\text{H}_2\text{O}$  and one mole of  $\text{C}_2\text{H}_2$ ,

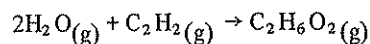
$$\Delta H = \sum nH_{(p)} - \sum nH_{(r)}$$

$$\Delta H = [(2 \text{ mol}) (-285.8 \text{ kJ mol}^{-1}) + (1 \text{ mol}) (226.8 \text{ kJ mol}^{-1})] - [(1 \text{ mol}) (-528.4 \text{ kJ mol}^{-1})]$$

$$\Delta H = 183.6 \text{ kJ}$$

The reaction is endothermic.

- Q-35 What is the enthalpy change for the reaction

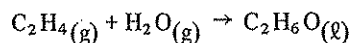


Is the reaction endothermic or exothermic?

A-35  $\Delta H_{(\text{forward})} = -\Delta H_{(\text{reverse})}$

Therefore,  $\Delta H = -183.6 \text{ kJ}$ , and the reaction is exothermic.

- Q-36 What is the enthalpy of  $\text{C}_2\text{H}_6\text{O}_{(g)}$  if the enthalpy change for the reaction



is  $-87.9 \text{ kJ}$  and

$$H_{\text{C}_2\text{H}_4_{(g)}} = 52.3 \text{ kJ mol}^{-1}$$

$$H_{\text{H}_2\text{O}_{(g)}} = -241.8 \text{ kJ mol}^{-1}$$

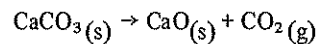
A-36  $\Delta H = \sum nH_{(p)} - \sum nH_{(r)}$

$$-87.9 \text{ kJ} = [(1 \text{ mol}) (H_{\text{C}_2\text{H}_6\text{O}})] - [(1 \text{ mol}) (52.3 \text{ kJ mol}^{-1}) + (1 \text{ mol}) (-241.8 \text{ kJ mol}^{-1})]$$

$$H_{\text{C}_2\text{H}_6\text{O}_{(g)}} = \frac{-87.9 \text{ kJ} + 52.3 \text{ kJ} - 241.8 \text{ kJ}}{1 \text{ mol}}$$

$$= -277.4 \text{ kJ mol}^{-1}$$

- Q-37 What is the enthalpy of  $\text{CaCO}_3_{(s)}$  if the enthalpy change for the reaction



is  $178.2 \text{ kJ}$  and

$$H_{\text{CO}_2_{(g)}} = -393.3 \text{ kJ mol}^{-1}$$

$$H_{\text{CaO}_{(s)}} = -635.1 \text{ kJ mol}^{-1}$$

A-37  $\Delta H = \sum nH_{(p)} - \sum nH_{(r)}$

$$178.2 \text{ kJ} = [(1 \text{ mol}) (-393.3 \text{ kJ mol}^{-1}) + (1 \text{ mol}) (-635.1 \text{ kJ mol}^{-1})] - [(1 \text{ mol}) (H_{\text{CaCO}_3})]$$

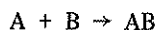
$$H_{\text{CaCO}_3_{(s)}} = \frac{-178.2 \text{ kJ} - 393.3 \text{ kJ} - 635.1 \text{ kJ}}{1 \text{ mol}}$$

$$= -1207 \text{ kJ mol}^{-1}$$

- R
- a)  $\Delta H = \sum nH_{(p)} - \sum nH_{(r)}$
  - b)  $\Delta H = \text{negative}$  (exothermic reaction)
  - c)  $\Delta H = \text{positive}$  (endothermic reaction)
  - d)  $\Delta H_{(\text{forward})} = -\Delta H_{(\text{reverse})}$

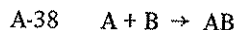
- S-5 How is the enthalpy of a compound determined? Just as a date is relative to some reference point, i.e., 1974 A.D. equals 1974 years after the reference point and 376 B.C. equals 376 years before the reference point, the enthalpy of a substance is relative to a reference point. No absolute value of time is known and no absolute value of enthalpy is implied. The A.D. and the B.C. from the dates become + and - in scientific notation.

The enthalpy of a compound is equal to the enthalpy change of the reaction for the formation of the compound from its pure elements. This enthalpy change is called the heat of formation of the compound.



$$\Delta H_f = \text{heat of formation} = H_{AB}$$

- Q-38 From the definition of enthalpy of a compound, what can be said about the enthalpy of a pure element?



$$\Delta H = \sum n H_{(p)} - \sum n H_{(r)}$$

$$\Delta H = H_{AB} - H_A - H_B$$

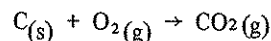
$$\Delta H = \text{heat of formation} = \Delta H_f$$

$$\Delta H_f = H_{AB}$$

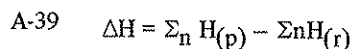
$$\text{Therefore, } H_A = -H_B$$

The only way this expression can always be valid is for both  $H_A$  and  $H_B$  to be equal to zero. Thus, the enthalpy of an element in its standard state is by convention equal to zero. The pure elements are taken as reference states.

- Q-39 The enthalpy change for the reaction



is equal to -393.3 kJ. What is the enthalpy of  $CO_2$ ?

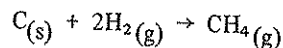


$$\Delta H = [(1 \text{ mol}) (H_{CO_2})] - [(1 \text{ mol}) (H_C) + (1 \text{ mol}) (H_{O_2})]$$

$$H_C = H_{O_2} = 0$$

$$H_{CO_2} = \frac{\Delta H}{1 \text{ mol}} = \Delta H_f = -393.3 \text{ kJ mol}^{-1}$$

- Q-40 The enthalpy change for the reaction



is equal to -74.9 kJ. What is the enthalpy of  $CH_4$ ?

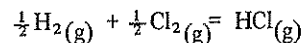
A-40  $\Delta H = \sum nH_{(p)} - \sum nH_{(r)}$

$$\Delta H = [(1 \text{ mol}) (H_{\text{CH}_4})] - [(2 \text{ mol}) (H_{\text{H}_2}) + (1 \text{ mol}) (H_{\text{C}})]$$

$$H_{\text{H}_2} = H_{\text{C}} = 0$$

$$H_{\text{CH}_4(g)} = \frac{\Delta H}{1 \text{ mol}} = \Delta H_f = -74.9 \text{ kJ mol}^{-1}$$

Q-41 What is the enthalpy change for the reaction



$$\text{if } \Delta H_f = H_{\text{HCl}} = -92.5 \text{ kJ mol}^{-1} ?$$

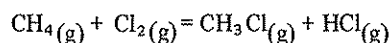
A-41  $\Delta H = \sum nH_{(p)} - \sum nH_{(r)}$

$$\Delta H = [(1 \text{ mol}) (H_{\text{HCl}})] - [0 + 0]$$

$$H_{\text{HCl}} = \Delta H_f = -92.5 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta H &= (1 \text{ mol}) (-92.5 \text{ kJ mol}^{-1}) \\ &= -92.5 \text{ kJ} \end{aligned}$$

Q-42 What is the enthalpy change for the reaction



$$\text{if } \Delta H_f(\text{CH}_4) = -74.9 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{CH}_3\text{Cl}) = -83.7 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{HCl}) = -92.0 \text{ kJ mol}^{-1}$$

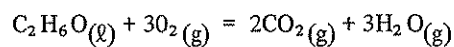
A-42  $\Delta H = \sum n\Delta H_{f(p)} - \sum n\Delta H_{f(r)}$

$$\Delta H = [(1 \text{ mol}) (\Delta H_f(\text{CH}_3\text{Cl})) + (1 \text{ mol}) (\Delta H_f(\text{HCl}))] - [(1 \text{ mol}) (H_{\text{Cl}_2}) + (1 \text{ mol}) (\Delta H_f(\text{CH}_4))]$$

$$\Delta H = [(1 \text{ mol}) (-83.7 \text{ kJ mol}^{-1}) + (1 \text{ mol}) (-92.0 \text{ kJ mol}^{-1})] -$$

$$\Delta H = -100.8 \text{ kJ} \quad [ (1 \text{ mol}) (0) + (1 \text{ mol}) (-74.9 \text{ kJ mol}^{-1}) ]$$

Q-43 What is the enthalpy change for the reaction



$$\text{if } \Delta H_f(\text{C}_2\text{H}_6\text{O}) = -277.4 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{CO}_2) = -393.3 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{H}_2\text{O}) = -285.8 \text{ kJ mol}^{-1}$$

$$\text{A-43} \quad \Delta H = \sum n \Delta H_f(p) - \sum n \Delta H_f(r)$$

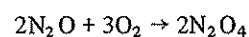
$$\Delta H = [(2 \text{ mol}) (\Delta H_f(\text{CO}_2)) + (3 \text{ mol}) (\Delta H_f(\text{H}_2\text{O}))] - [(3 \text{ mol}) (\Delta H_f(\text{H}_2\text{O}_2)) + (1 \text{ mol}) (\Delta H_f(\text{C}_2\text{H}_6))]$$

$$\Delta H = [(2 \text{ mol}) (-393.3 \text{ kJ mol}^{-1}) + (3 \text{ mol}) (-285.8 \text{ kJ mol}^{-1})] - [0 + (1 \text{ mol}) (277.4 \text{ kJ mol}^{-1})]$$

$$\Delta H = -1366 \text{ kJ}$$

Q-44 The  $\Delta H_f$  for a compound depends on the temperature at which the reaction takes place. In tables of thermodynamic data (see Table I), the heats of formation are given for the compound at 25 °C and 101.3 kN m<sup>-2</sup> (1 atm pressure). This is called the standard heat of formation,  $\Delta H_f^\circ$ .

What is the enthalpy change at 25 °C for the reaction



$$\text{if } \Delta H_f^\circ(\text{N}_2\text{O}) = 81.6 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(\text{N}_2\text{O}_4) = 9.6 \text{ kJ mol}^{-1}$$

$$\text{A-44} \quad \Delta H = \sum n \Delta H_f(p) - \sum n \Delta H_f(r)$$

$$\text{at } 25^\circ\text{C} \quad \Delta H_f = \Delta H_f^\circ$$

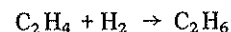
$$\Delta H = [(2 \text{ mol}) (\Delta H_f^\circ(\text{N}_2\text{O}_4))] - [(3 \text{ mol}) (\Delta H_f^\circ(\text{H}_2\text{O}_2)) + (2 \text{ mol}) (\Delta H_f^\circ(\text{N}_2\text{O}))]$$

$$\Delta H = [(2 \text{ mol}) (9.6 \text{ kJ mol}^{-1})] - [0 + (2 \text{ mol}) (81.6 \text{ kJ mol}^{-1})]$$

$$\Delta H = -143.9 \text{ kJ} = \Delta H^\circ$$

( $\Delta H^\circ$  is the enthalpy change for the reaction at standard conditions, 101.3 kN m<sup>-2</sup> pressure and 25 °C.)

Q-45 What is the enthalpy change at 25 °C for the reaction



$$\Delta H_f^\circ(\text{C}_2\text{H}_4) = 52.3 \text{ kJ mol}^{-1}$$

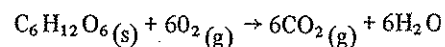
$$\Delta H_f^\circ(\text{C}_2\text{H}_6) = -84.5 \text{ kJ mol}^{-1}$$

$$\text{A-45} \quad \Delta H^\circ = \sum n \Delta H_f^\circ(p) - \sum n \Delta H_f^\circ(r)$$

$$\Delta H^\circ = [(1 \text{ mol}) (-84.5 \text{ kJ mol}^{-1})] - [(1 \text{ mol}) (0) + (1 \text{ mol}) (52.3 \text{ kJ mol}^{-1})]$$

$$\Delta H^\circ = -136.8 \text{ kJ}$$

Q-46 Man has the ability to use the chemical energy stored by plants for body processes. Glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , is one plant material utilized by man. Calculate the heat produced,  $\Delta H^\circ$ , when one mole of glucose is metabolized at 25 °C by the reaction



$$\Delta H_f^\circ(\text{C}_6\text{H}_{12}\text{O}_6) = 1275.1 \text{ kJ mol}^{-1}$$

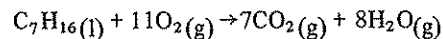
See Q-43 for other data

A-46  $\Delta H^\circ = \sum n \Delta H_f^\circ(\text{p}) - \sum n \Delta H_f^\circ(\text{r})$

$$\Delta H^\circ = [(6 \text{ mol}) (-285.9 \text{ kJ mol}^{-1}) + (6 \text{ mol}) (-393.5 \text{ kJ mol}^{-1})] - [(6 \text{ mol}) (0) + (1 \text{ mol}) (-1275.1 \text{ kJ mol}^{-1})]$$

$$\begin{aligned} \Delta H^\circ &= (-1715.4) + (-2361.0) - (-1275.1) \\ &= -2801.3 \text{ kJ} \end{aligned}$$

Q-47 Heptane,  $\text{C}_7\text{H}_{16}$ , can be used as an approximation for the composition of gasoline. Calculate the enthalpy change at  $25^\circ\text{C}$  for the combustion of one mole of heptane. The combustion reaction is



$$\Delta H_f^\circ(\text{C}_7\text{H}_{16}) = -198.9 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(\text{CO}_2) = -393.5 \text{ kJ mol}^{-1}$$

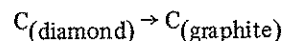
$$\Delta H_f^\circ(\text{H}_2\text{O}) = -285.9 \text{ kJ mol}^{-1}$$

A-47  $\Delta H^\circ = \sum n \Delta H_f^\circ(\text{p}) - \sum n \Delta H_f^\circ(\text{r})$

$$\Delta H^\circ = [(8 \text{ mol}) (-285.9 \text{ kJ mol}^{-1}) + (7 \text{ mol}) (-393.5 \text{ kJ mol}^{-1})] - [(11 \text{ mol}) (0) + (1 \text{ mol}) (-198.9 \text{ kJ mol}^{-1})]$$

$$\begin{aligned} \Delta H^\circ &= (-2287.2) + (-2754.5) - (-198.9) \\ &= -4843 \text{ kJ} \end{aligned}$$

Q-48 Consider the reaction for the transition of carbon in the diamond form to carbon in the graphite form.



$$\Delta H^\circ = -1.90 \text{ kJ J}$$

From an energy point of view alone, which form of carbon is more stable at  $25^\circ\text{C}$ ?

A-48 Graphite

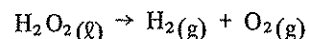
$$\Delta H^\circ = H_C^\circ(\text{graphite}) - H_C^\circ(\text{diamond})$$

Since  $\Delta H^\circ$  is negative for the reaction,

$H_C^\circ(\text{diamond})$  is greater than  $H_C^\circ(\text{graphite})$ .

Therefore, the graphite form is at lower energy making it more stable.

Q-49 The decomposition of hydrogen peroxide into its constituent elements according to the reaction



is endothermic by  $187.9 \text{ kJ mol}^{-1}$ . What conclusion can be made about the stability of hydrogen peroxide with respect to the elements?



<p>A-49 Since heat is necessary to convert hydrogen peroxide into the elements, hydrogen peroxide is energetically <u>more stable</u> with respect to the elements.</p>	<p>Q-50 The decomposition of hydrogen peroxide by the reaction</p> $\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g})$ <p>is exothermic by <math>97.9 \text{ kJ mol}^{-1}</math>. What conclusion can be made about the stability of hydrogen peroxide with respect to decomposition into water and oxygen?</p>
<p>A-50 Since heat is given off when hydrogen peroxide decomposes into water and oxygen, hydrogen peroxide is energetically <u>less stable</u> with respect to the decomposition products.</p>	<p>Q-51 From a consideration of the last two problems, what information is needed to say whether a substance is stable or unstable?</p>
<p>A-51 It is useful to talk about stability only in terms of the possible decomposition products.</p>	<p>Q-52 The enthalpies of formation for <math>\text{SO}_2</math> and <math>\text{NO}_2</math> are <math>297.1 \text{ kJ mol}^{-1}</math> and <math>33.9 \text{ kJ mol}^{-1}</math>, respectively. Which compound is more stable with respect to the elements? Why?</p>
<p>A-52 <math>\text{SO}_2</math>. The reaction for the decomposition of <math>\text{SO}_2</math> is endothermic by <math>297.1 \text{ kJ mol}^{-1}</math> while the decomposition of <math>\text{NO}_2</math> is exothermic by <math>33.9 \text{ kJ mol}^{-1}</math>. For an endothermic reaction, <math>\Delta H = +</math>. The products are at a higher energy than the reactants; therefore, the reactants are more stable.</p>	<p>Q-53 The enthalpies of formation for <math>\text{CaO}</math> and <math>\text{BaO}</math> are <math>-635.1 \text{ kJ mol}^{-1}</math> and <math>-558.6 \text{ kJ mol}^{-1}</math>, respectively. Which compound is more stable with respect to the elements? Why?</p>
<p>A-53 <math>\text{CaO}</math>. The reaction for the decomposition of <math>\text{CaO}</math> into its elements is endothermic by <math>635.1 \text{ kJ mol}^{-1}</math> while the decomposition of <math>\text{BaO}</math> into its elements is endothermic by only <math>558.6 \text{ kJ mol}^{-1}</math>. Thus, more energy is released in the formation of <math>\text{CaO}</math>, resulting in a lower energy (more stable) product.</p>	<p><b>Q-54</b> Given the following standard enthalpies of formation</p> $\Delta H_f^\circ(\text{O}_3)(\text{g}) = +142.2 \text{ kJ mol}^{-1}$ $\Delta H_f^\circ(\text{CO}_2)(\text{g}) = -393. \text{ kJ mol}^{-1}$ $\Delta H_f^\circ(\text{NH}_3)(\text{g}) = -46.2 \text{ kJ mol}^{-1}$ $\Delta H_f^\circ(\text{HI})(\text{g}) = +25.9 \text{ kJ mol}^{-1}$ <p>arrange the compounds in the order of increasing stability with respect to decomposition into their elements.</p>

A-54 least stable  $\rightarrow$  most stable  
 $\text{O}_3, \text{HI}, \text{NH}_3, \text{CO}_2$

Q-55 Which of the two isomers of butane ( $\text{C}_4\text{H}_{10}$ ) is more stable at  $25^\circ\text{C}$ ?

<u>isomer</u>	<u><math>\Delta H_f^\circ</math></u>
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n-butane  
 $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3) -124.7 \text{ kJ mol}^{-1}$

isobutane  
 $(\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3) -131.4 \text{ kJ mol}^{-1}$

A-55 Isobutane. It has the higher negative value for enthalpy of formation.

Q-56 Consider the reaction

n-butane  $\rightarrow$  isobutane.

What is the enthalpy change for this reaction? Is the reaction exothermic or endothermic? How does your answer confirm the relative stabilities of these two compounds?

A-56  $\Delta H^\circ = \sum n\Delta H_f^\circ(\text{p}) - \sum n\Delta H_f^\circ(\text{r})$

$$\Delta H^\circ = [(1 \text{ mol})(-131.4 \text{ kJ mol}^{-1})] - [(1 \text{ mol})(-124.7 \text{ kJ mol}^{-1})]$$

$$\Delta H^\circ = -131.4 - (-124.7) = -6.7 \text{ kJ}$$

The reaction is exothermic; thus, isobutane is at lower energy and is more stable.

Q-57 Which isomer of pentane ( $\text{C}_5\text{H}_{12}$ ) is the most stable at  $25^\circ\text{C}$  in terms of energy only?

<u>isomer</u>	<u><math>\Delta H_f^\circ</math></u>
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n-pentane  
 $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3) -146.4 \text{ kJ mol}^{-1}$

neopentane  
 $((\text{CH}_3)_4\text{C}) -166.1 \text{ kJ mol}^{-1}$

isopentane  
 $(\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)_2) -154.4 \text{ kJ mol}^{-1}$

A-57 Neopentane. This isomer has the lowest enthalpy value.

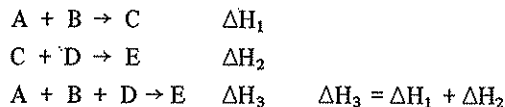
R a)  $\Delta H_f^\circ(\text{AB}) =$  standard enthalpy of formation at  $25^\circ\text{C}$  and  $101.3 \text{ kN m}^{-2}$  pressure  
 $= H^\circ(\text{AB})$

b)  $H_{\text{(element)}}^\circ = 0$  (by convention)

c)  $\Delta H^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum n\Delta H_f^\circ(\text{reactants})$

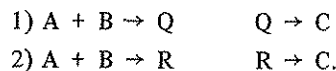
d) Superscript zero indicates standard state ( $101.3 \text{ kN m}^{-2}$  and  $25^\circ\text{C}$ ).

- S-6 If a reaction can be carried out by a series of steps, the overall enthalpy change is the sum of the enthalpy changes of the individual steps. In mathematical terms this becomes



This relationship is known as Hess's Law.

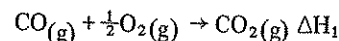
- Q-58 Consider two processes, both of which produce C from A and B but which differ by the intermediate formed:



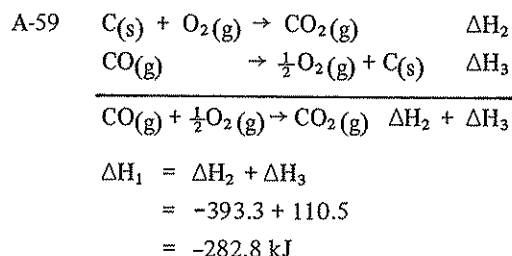
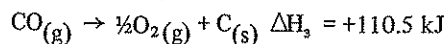
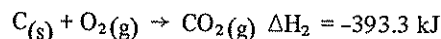
Will the enthalpy change for process 1 be the same as the enthalpy change for process 2?

- A-58 Yes. The enthalpy change by either path must be identical since the overall reaction is the same.

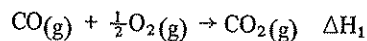
- Q-59 Calculate the enthalpy change for the reaction



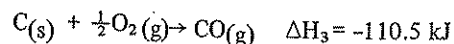
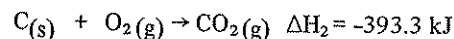
from the enthalpy changes for the reactions



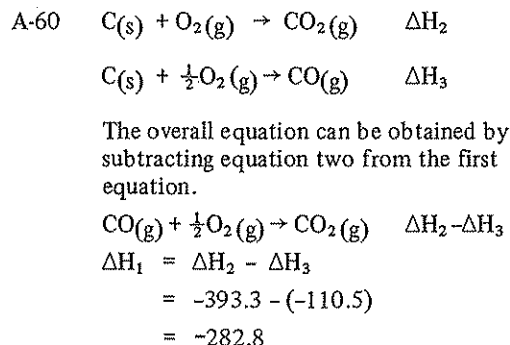
- Q-60 Calculate the enthalpy change for the reaction



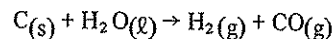
from the  $\Delta H$  changes for the reactions



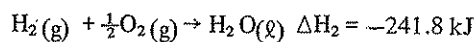
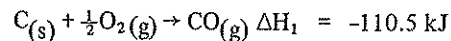
Equations can be subtracted as well as added.



- Q-61 Compute the  $\Delta H$  of the reaction



from the enthalpy changes of the reactions



- A-61 By subtracting the second equation from the first, the desired reaction is obtained.

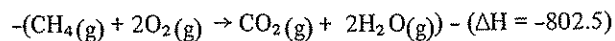
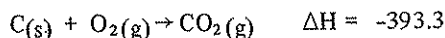
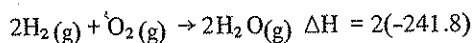
$$\begin{aligned}\Delta H &= \Delta H_1 - \Delta H_2 \\ &= -110.5 - (-241.8) \\ &= 131.3 \text{ kJ}\end{aligned}$$

A-62 
$$\Delta H = \frac{-110.5 \text{ kJ}}{\text{mol of CO formed}} \times \frac{2 \text{ mol}}{1} = -221.0 \text{ kJ}$$

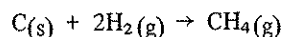
- A-63 In order to obtain the desired reaction the second equation must be multiplied by two and subtracted from the first.

$$\begin{aligned}\Delta H &= \Delta H_1 - 2(\Delta H_2) \\ &= -641.0 - 2(-92.5) \\ &= -456.0 \text{ kJ}\end{aligned}$$

- A-64 The desired reaction can be obtained by doubling reaction 3 and subtracting the first reaction from the sum of the last two.



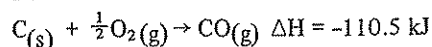
Adding these yields



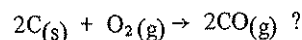
$$H_{\text{CH}_4} = \Delta H_f = \frac{\Delta H}{\text{mol}}$$

$$\begin{aligned}&= 2(-241.8) - 393.3 - (-802.5) \\ &= -74.4 \text{ kJ mol}^{-1}\end{aligned}$$

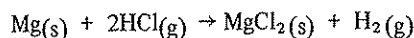
- Q-62 For the reaction



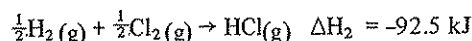
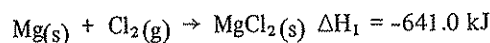
What is the enthalpy change for the reaction



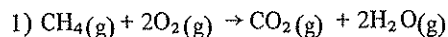
- Q-63 Find  $\Delta H$  for the reaction



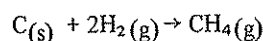
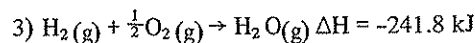
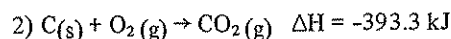
from



- Q-64 Find the enthalpy of methane ( $\text{CH}_4$ ) from

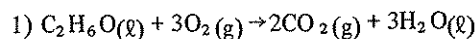


$$\Delta H = -802.5 \text{ kJ}$$

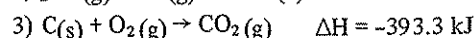
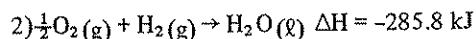


$$\Delta H_f = H_{\text{CH}_4}$$

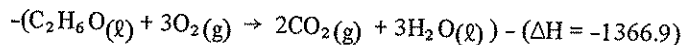
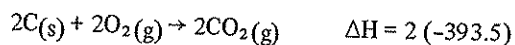
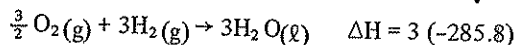
- Q-65 Calculate the enthalpy (heat of formation) for ethyl alcohol ( $\text{C}_2\text{H}_6\text{O}$ ) from the enthalpy of combustion of ethyl alcohol.



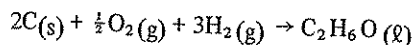
$$\Delta H = -1366.9 \text{ kJ}$$



- A-65 The desired reaction can be obtained by adding three times the second reaction to two times the third reaction and subtracting the first reaction.

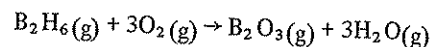


This gives:

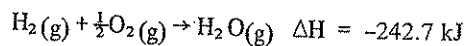
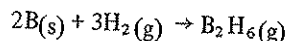


$$\begin{aligned} H_{\text{C}_2\text{H}_6\text{O}} = \Delta H_f &= \frac{\Delta H}{1 \text{ mol}} \\ &= 3(-285.8) + 2(-393.3) - (-1366.9) \\ &= -277.1 \text{ kJ mol}^{-1} \end{aligned}$$

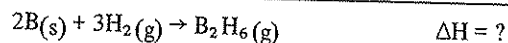
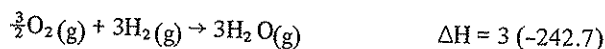
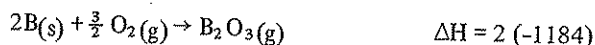
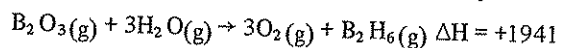
- Q-66 Combustion of diborane,  $\text{B}_2\text{H}_6$ , proceeds according to the equation



and 1941 kJ are liberated per mole of  $\text{B}_2\text{H}_6$ . Combustion of boron metal also proceeds to the product  $\text{B}_2\text{O}_3$  and liberates 1184 kJ  $\text{mol}^{-1}$  of boron used. What is the enthalpy change for the reaction



- A-66 The desired reaction can be obtained by adding the following equations

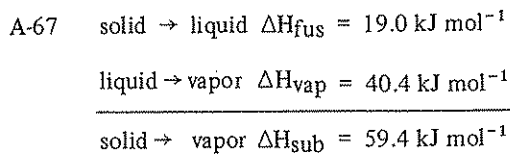


$$\begin{aligned} \Delta H &= 1941 + 2(-1184) + 3(-242.7) \\ &= -1154 \text{ kJ} \end{aligned}$$

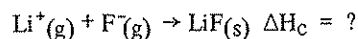
- Q-67 Calculate the heat of sublimation,  $\Delta H_{\text{sub}}$ , for naphthalene (moth balls) from a knowledge of the heat of fusion,  $\Delta H_{\text{fus}}$ , and the heat of vaporization,  $\Delta H_{\text{vap}}$ .

$$\Delta H_{\text{fus}} = 19.0 \text{ kJ mol}^{-1}$$

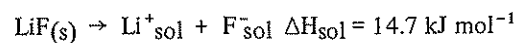
$$\Delta H_{\text{vap}} = 40.4 \text{ kJ mol}^{-1}$$



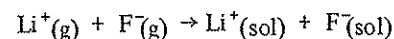
Q-68    Calculate the crystal energy,  $\Delta H_c$ , for LiF which is represented by the reaction



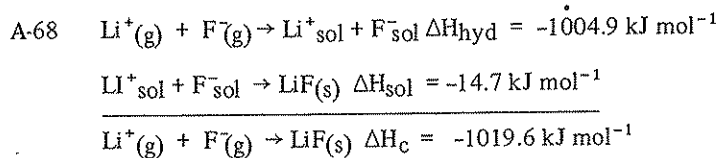
The heat of solution of LiF(s) is given by the equation



and the heat of hydration of the gaseous ions is given by the equation



$$\Delta H_{\text{hyd}} = -1004.9 \text{ kJ mol}^{-1}$$



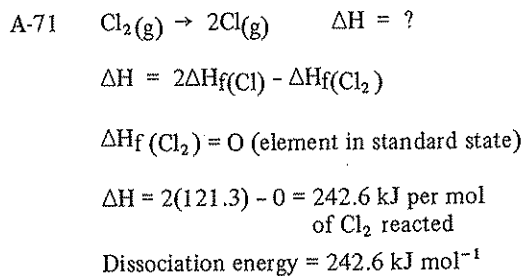
Q-69    The enthalpy change for the reaction  $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$  is + 436 kJ. This reaction is endothermic. What is the absorbed energy used for in this reaction?

A-69    The energy absorbed in the reaction is used to break the H—H bond. This is called the dissociation energy of the hydrogen molecule.

Q-70    The enthalpy change for the reaction  $\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$  is 494.6 kJ per mol of  $\text{O}_2$  reacted. What is the dissociation energy of the  $\text{O}_2$  molecule?

A-70    494.6 kJ

Q-71    What is the dissociation energy for the chlorine molecule if  $\Delta H_f(\text{Cl})$  is 121.3 kJ  $\text{mol}^{-1}$ ?

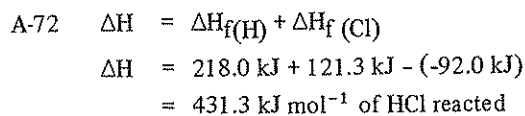


Q-72    What is the dissociation energy of HCl if

$$\Delta H_f(\text{HCl}_g) = -92.0 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{H}) = 218.0 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{Cl}) = 121.3 \text{ kJ mol}^{-1}$$



This is the energy necessary to break the H—Cl bond.

Q-73    What is the dissociation energy of ICl if

$$\Delta H_f(\text{ICl}_g) = 17.6 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{Cl}) = 121.3 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{I}) = 106.7 \text{ kJ mol}^{-1}$$

A-73  $\Delta H = \Delta H_f(I) + \Delta H_f(Cl) - \Delta H_f(ICl)$   
 $= 106.7 + 121.3 - (17.6)$   
 $= 210.4 \text{ kJ mol}^{-1}$  of ICl reacted

This is the energy necessary to break the I—Cl bond.

**Q-74** What is the relationship between bond energy and dissociation energy for a diatomic molecule?

A-74 They are the same.

- R a)  $A + B \rightarrow C \quad \Delta H_1$   
 $A \rightarrow Q \quad \Delta H_2$   
 $Q + B \rightarrow C \quad \Delta H_3$   
 Hess's Law:  $\Delta H_1 = \Delta H_2 + \Delta H_3$   
 b) Dissociation energy for a diatomic molecule is equal to the bond energy.  
 c)  $AB \rightarrow A + B \quad \Delta H = \text{dissociation energy.}$

S-7 The dissociation energy and bond energy are not identical for polyatomic molecules (molecules with three or more atoms). For example, consider the  $H_2O$  molecule. One dissociation step would be



The second dissociation step would be

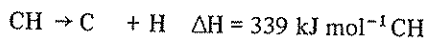
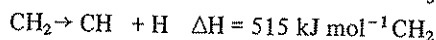
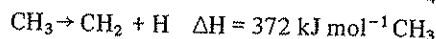
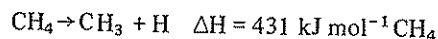


The O—H bond energy would be defined as the average of these two values.

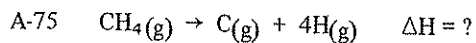
$$\epsilon_{OH} = \frac{501.7 + 423.4}{2} = 462.6 \text{ kJ per mol of OH bonds}$$

The dissociation energy is the energy required to break a given bond of some specific compound. Bond energy is an average value of the dissociation energies of a given bond in a series of different dissociating species.

**Q-75** Calculate the C—H bond energy from the following dissociation energies.



All species are in the gaseous state.



$$\text{bond energy } (\epsilon_{C-H}) = \frac{\Delta H}{4}$$

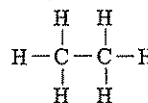
The above equation may be obtained by adding the four equations together. Therefore,

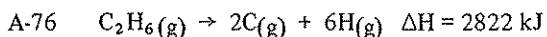
$$\Delta H = 431 + 372 + 515 + 339$$

$$= 1657 \text{ kJ mol}^{-1}$$

$$\epsilon_{C-H} = \frac{1657}{4} = 414.1 \text{ kJ mol}^{-1}$$

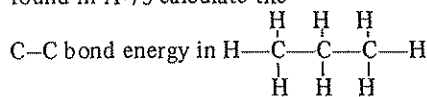
**Q-76** The sum of the dissociation energies for  $C_2H_6$  dissociating into its elements is  $2822 \text{ kJ mol}^{-1}$ . With the value of  $\epsilon_{C-H}$  found for methane, calculate the C—C bond energy in ethane.



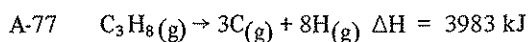


Six C—H bonds were broken,  $414 \text{ kJ mol}^{-1}$  for each bond. Total for six =  $2484 \text{ kJ mol}^{-1}$ . Subtracting gives  $2822 - 2484 = 338 \text{ kJ mol}^{-1}$ . This equals  $\epsilon_{\text{C—C}}$  or the energy to break the C—C bond.

Q-77 The sum of the dissociation energies for  $\text{C}_3\text{H}_8$  dissociating into its elements is  $3983 \text{ kJ mol}^{-1}$ . With the value of  $\epsilon_{\text{C—H}}$  found in A-75 calculate the



and compare with the value found for  $\text{C}_2\text{H}_6$ .

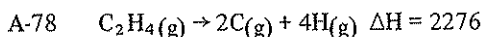
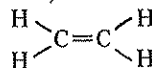


Eight C—H bonds were broken at  $414 \text{ kJ mol}^{-1}$  each, total for 8 =  $3312 \text{ kJ mol}^{-1}$ . Therefore,  $3983 - 3312 = 671 \text{ kJ mol}^{-1}$  = energy necessary to break two C—C bonds.

$$\epsilon_{\text{C—C}} = \frac{671}{2} = 335 \text{ kJ mol}^{-1} \text{ which is the}$$

energy necessary to break one C—C bond. This value is approximately the same as that calculated from  $\text{C}_2\text{H}_6$ .

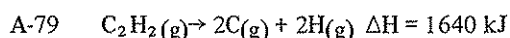
Q-78 The sum of the dissociation energies for  $\text{C}_2\text{H}_4$  dissociating into its elements is  $2276 \text{ kJ mol}^{-1}$ . With the value of  $\epsilon_{\text{C—H}}$  found in A-75, calculate the C = C bond energy in



Four C—H bonds were broken at  $414 \text{ kJ mol}^{-1}$  of each bond: total for 4 =  $1657 \text{ kJ mol}^{-1}$ . Therefore,  $2276 - 1657 = 619 \text{ kJ mol}^{-1} = \epsilon_{\text{C}=\text{C}}$

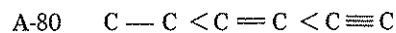
which is the energy necessary to break one C=C bond.

Q-79 The sum of the dissociation energies for  $\text{C}_2\text{H}_2$  dissociating into its elements is  $1640 \text{ kJ mol}^{-1}$ . With the value of  $\epsilon_{\text{C—H}}$  found in A-75, calculate the C  $\equiv$  C bond energy in  $\text{H}-\text{C}\equiv\text{C}-\text{H}$ .



Two C—H bonds were broken for a total energy of  $828 \text{ kJ mol}^{-1}$ . Therefore,  $\epsilon_{\text{C}\equiv\text{C}} = 1640 - 828 = 812 \text{ kJ mol}^{-1}$  which is the energy necessary to break one C  $\equiv$  C bond.

Q-80 List the following in order of increasing bond strength: C  $\equiv$  C, C — C, C = C.



Q-81 What general statement can be made relating bond strength to bond order, i.e., single, double, triple?

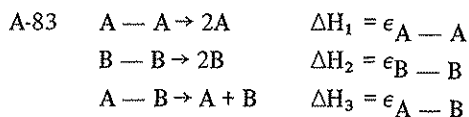
A-81 The higher the bond order the greater the bond strength.

Q-82 In the reaction  $2\text{Cl}_2(\text{g}) + \text{C}(\text{g}) \rightarrow \text{CCl}_4(\text{g})$  what bonds are being made and what bonds broken?

A-82 Two Cl — Cl bonds are being broken and four C — Cl bonds are being formed.

Q-83 Show that  $\Delta\text{H}$  for the reaction  
 $\text{A—A} + \text{B—B} \rightarrow 2\text{A—B}$   
 is equal to ( $\Sigma$  energy of bonds being broken —  $\Sigma$  energy of bonds being formed).  
 Write  $\Delta\text{H}$  for the dissociation of each molecule.





Take twice the negative of the last reaction and add to the first two to get the overall enthalpy change (Hess's Law).

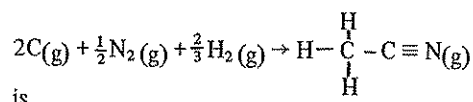
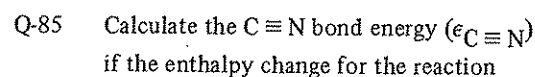
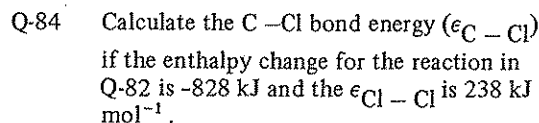
$$\begin{aligned}\Delta H &= \Delta H_1 + \Delta H_2 - 2\Delta H_3 \\ &= \epsilon_{A-A} + \epsilon_{B-B} - 2\epsilon_{A-B}\end{aligned}$$

Since  $\epsilon_{A-A} + \epsilon_{B-B}$  represents the total energy of bonds being broken and  $2\epsilon_{A-B}$  represents the total energy of bonds being formed,

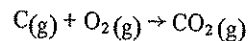
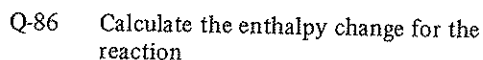
$$\Delta H = \Sigma \text{ energy of bonds being broken} - \Sigma \text{ energy of bonds being formed.}$$

A-84     $\Delta H = (\Sigma \text{ energy of bonds being broken}) - (\Sigma \text{ energy of bonds being formed})$   
 $-828 = 2(238) - 4(\epsilon_{C-Cl})$   
 $\epsilon_{C-Cl} = \frac{-828 - 476}{-4} = 326 \text{ kJ mol}^{-1}$

A-85     $\Delta H = (\Sigma \text{ energy of bonds broken}) - (\Sigma \text{ energy of bonds formed})$   
 $-1347 = \frac{1}{2}(941) + \frac{3}{2}(431) - [335 + 3(414) + \epsilon_{C \equiv N}]$   
 $\epsilon_{C \equiv N} = 887 \text{ kJ mol}^{-1}$



$$\begin{aligned}\Delta H &= -1347 \text{ kJ mol}^{-1} \\ \epsilon_{N \equiv N} &= 941 \text{ kJ mol}^{-1} \\ \epsilon_{H-H} &= 431 \text{ kJ mol}^{-1} \\ \epsilon_{C-C} &= 335 \text{ kJ mol}^{-1} \\ \epsilon_{C-H} &= 414 \text{ kJ mol}^{-1}\end{aligned}$$

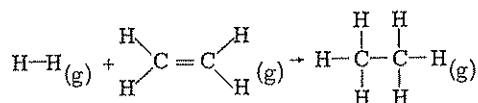


if the bond energies are

$$\begin{aligned}\epsilon_{O_2} &= 489 \text{ kJ mol}^{-1} \\ \epsilon_{C=O} &= 724 \text{ kJ mol}^{-1}\end{aligned}$$

A-86  $\Delta H = (\sum \epsilon_{\text{bonds broken}}) - (\sum \epsilon_{\text{bonds formed}})$   
 $= 489 - 2(724)$   
 $= -959 \text{ kJ}$

Q-87 Calculate the enthalpy change for the reaction



If the bond energies are

$$\epsilon_{\text{H}-\text{H}} = 431 \text{ kJ mol}^{-1}$$

$$\epsilon_{\text{C}=\text{C}} = 607 \text{ kJ mol}^{-1}$$

$$\epsilon_{\text{C}-\text{C}} = 335 \text{ kJ mol}^{-1}$$

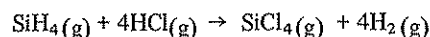
$$\epsilon_{\text{C}-\text{H}} = 414 \text{ kJ mol}^{-1}$$

A-87  $\Delta H = \epsilon_{\text{H}-\text{H}} + \epsilon_{\text{C}=\text{C}} - \epsilon_{\text{C}-\text{C}} - 2\epsilon_{\text{C}-\text{H}}$   
 $= 431 + 607 - 335 - 2(414)$   
 $= -125 \text{ kJ}$

Q-88 The experimental value for the enthalpy for the reaction in Q-87 is 137 kJ. Why might the calculated and the experimental values differ?

A-88 The bond energies used are average bond energies. The bond energy in a specific compound may differ from the average by several  $\text{kJ mol}^{-1}$ .

Q-89 Estimate the enthalpy change for the reaction



if the bond energies are

$$\epsilon_{\text{Si}-\text{H}} = 318 \text{ kJ mol}^{-1}$$

$$\epsilon_{\text{H}-\text{Cl}} = 431 \text{ kJ mol}^{-1}$$

$$\epsilon_{\text{Si}-\text{Cl}} = 364 \text{ kJ mol}^{-1}$$

$$\epsilon_{\text{H}-\text{H}} = 431 \text{ kJ mol}^{-1}$$

A-89  $\Delta H = 4\epsilon_{\text{Si}-\text{H}} + 4\epsilon_{\text{H}-\text{Cl}} - 4\epsilon_{\text{Si}-\text{Cl}} - 4\epsilon_{\text{H}-\text{H}}$   
 $= 4(318) + 4(431) - 4(364) - 4(431)$   
 $= -184 \text{ kJ}$

- R
- $\Delta H = (\sum \text{energy of bonds being broken}) - (\sum \text{energy of bonds formed})$
  - The greater the bond order, the larger the bond energy
  - Bond energy is an average value of the dissociation energies of a given bond in a series of different dissociating species.

S-8 A spontaneous reaction or process in thermodynamics is one which has the potential to proceed without the assistance of an external agency. In this statement nothing is implied about the rate or time of the reaction or process. What makes a reaction or process spontaneous?

Q-90 Consider a ball held above the ground. What will happen when the ball is released? Is this a spontaneous process?

A-90 The ball will drop. This is a spontaneous process.

Q-91 Consider a wheel on top of an incline. What will happen when it is released? Is this a spontaneous process?

A-91	The wheel will roll down the incline. This is a spontaneous process.	Q-92	Consider a river flowing down a hill. Is this a spontaneous process?
A-92	Yes.	Q-93	Can the reverse of the process indicated in Q-90, 91 and 92 occur by themselves?
A-93	No. A spontaneous process is of itself irreversible. It can only be reversed when work is done on the system.	Q-94	What do the processes in Q-90 to Q-92 have in common?
A-94	Each has a net decrease in potential energy in the direction of spontaneous change.	Q-95	The energy lost in the process described above can be lost in the form of heat or be converted to kinetic energy. If a chemical reaction is analogous to the process given above, what will be the criteria for a spontaneous reaction?
A-95	A decrease in potential energy which results in a release of heat.	Q-96	Will a spontaneous reaction be exothermic or endothermic?
A-96	Exothermic, $\Delta H = \text{negative}$	Q-97	The reaction of glucose with oxygen is spontaneous. Are the criteria of a spontaneous reaction given in A-95 met? (See Q-46)
A-97	Yes. $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$ $\Delta H^\circ = -2801 \text{ kJ}$ <p style="text-align: center;">exothermic</p>	Q-98	Would you predict the reaction of hydrogen gas with oxygen gas to be a spontaneous process at $25^\circ\text{C}$ ? $\Delta H_f(\text{H}_2\text{O}) = -286 \text{ kJ mol}^{-1}$
A-98	Yes. $\text{O}_2(\text{g}) + \text{H}_2(\text{g}) = 2\text{H}_2\text{O}(\ell)$ $\Delta H^\circ = \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{O}_2) - \Delta H_f(\text{H}_2)$ $\Delta H^\circ = -286 - 0 - 0$ $= -286 \text{ kJ}$ <p style="text-align: center;">exothermic</p>	Q-99	Is the freezing of liquid water a spontaneous process at $-5^\circ\text{C}$ ? Does it satisfy the criteria of a spontaneous reaction?
A-99	Yes. Heat is given off by liquid water when it freezes. Therefore, it is an exothermic process.	Q-100	When NaOH is dissolved in water the reaction is $\text{NaOH}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$ $\Delta H = -43.1 \text{ kJ mol}^{-1}$ <p>Does this reaction satisfy the criteria of a spontaneous reaction?</p>

A-100 Yes. The dissolving of NaOH in  $H_2O$  is an exothermic process.

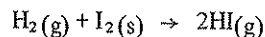
Q-101 Does ice melt at  $5^\circ C$ ? Does this meet the requirement for a spontaneous process?

A-101 It does melt. In melting ice absorbs heat. Therefore, melting is an endothermic process. Something is wrong with our criteria of a spontaneous process.

Q-102 When  $NH_4NO_3$  dissolves in water, the heat of solution is  $\Delta H = +26.5 \text{ kJ mol}^{-1}$ . Does this meet the requirements for a spontaneous process?

A-102 No. The dissolving of the  $NH_4NO_3$  in water is a spontaneous process which is endothermic. Another exception!

Q-103 The reaction



has an enthalpy change,  $\Delta H$ , equal to  $+53.5 \text{ kJ mol}^{-1}$ . Would you predict this to be a spontaneous reaction?

A-103 No. However, this is a spontaneous reaction. Another wrong prediction. While the decrease in energy may be a contributory factor to the driving force behind reactions and processes, it is NOT a sufficient one for all cases. We must look for another criterion for predicting spontaneous processes.

R  $\Delta H$  values alone are not reliable for predicting whether a reaction or process will be spontaneous.

S-9 While the First Law of Thermodynamics states the need for conservation of energy in a system, it does not allow us to predict the direction in which a process will occur spontaneously. The Second Law of Thermodynamics, which will be developed over the next several sections, will permit us to make a prediction about the spontaneity of a system.

Another factor which determines whether a chemical reaction will take place is the change in entropy,  $S$ , of a system. Entropy is the measure of the "degree of disorder" of a system. The greater the degree of disorder of a system, the higher will be the entropy of the system.

Q-104 Consider four coins. How many ways can the coins be arranged so that all the coins will be heads or all the coins will be tails?

A-104 There is only one way to arrange the coins so that they are all heads or all tails.

H	H	H	H
(1)	(2)	(3)	(4)

Q-105 How many ways can the coins be arranged so that there will be one head and three tails? Illustrate.

A-105 Four.

H	T	T	T
T	H	T	T
T	T	H	T
T	T	T	H
(1)	(2)	(3)	(4)

Q-106 How many ways can the coins be arranged so that there will be two heads and two tails? Illustrate.

A-106 Six.

H	H	T	T
H	T	H	T
H	T	T	H
T	H	H	T
T	H	T	H
T	T	H	H
(1)	(2)	(3)	(4)

Q-107 How many ways can the coins be arranged so that there will be one tail and three heads? Illustrate.

A-107 Four.

T	H	H	H
H	T	H	H
H	H	T	H
H	H	H	T
(1)	(2)	(3)	(4)

Q-108 The four coins are placed in a box. The box is shaken and a record is kept of how many heads and tails appear after each shaking. This process was repeated a thousand times. Which arrangement of coins will appear the most times?

A-108 Two heads and two tails. This is called the most probable arrangement.

Q-109 Which arrangement of coins has the least probability?

A-109 All heads or all tails. There is only one way of obtaining these arrangements.

Q-110 The higher the probability, the greater is the degree of disorder of the system. Which arrangement of coins will give the greatest degree of disorder?

A-110 Two heads and two tails. There are more ways to arrange the coins to get two heads and two tails than any other arrangement.

Q-111 Which arrangement of the coins has the most order?

A-111 All heads or all tails. There is only one way to obtain these arrangements.

Q-112 Remembering the relationship between degree of disorder and entropy, which arrangement of the coins has the greatest entropy? Why?

A-112 Two heads and two tails. This arrangement has the highest probability.

Q-113 Which arrangement of the coins has the smallest entropy? Why?

A-113 All heads or all tails. This arrangement has the lowest probability.

Q-114 A change in entropy of a system is defined as  $\Delta S = S_{\text{final}} - S_{\text{initial}}$ . If the four coins in a box are arranged so that they are all heads and the box is shaken, the arrangement of the coins might change to three heads and one tail or maybe two heads and two tails. What is the entropy change,  $\Delta S$ , for this process? Is it positive, negative or is there no change? Why?

A-114 positive

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

$$S_{\text{final}} > S_{\text{initial}}$$

Q-115 In the above change, does the system go to a more disordered state or a more ordered state?

A-115 A more disordered state.

Q-116 What is the relationship between the change in entropy and the change in order for a system going from one state to another?

A-116 A positive entropy change is associated with a system going to a more disordered state. A negative entropy change is associated with a system going to a more ordered state.

Q-117 In the example of the coins,  
4 heads  $\rightarrow$  2 heads + 2 tails  
the energy of the system remains constant. (The energy of each coin is the same whether a head or tail is showing.) As long as the energy remains constant ( $\Delta H = 0$ ), the entropy is a measure of the spontaneity of a process. If  $\Delta S$  is positive, the process is spontaneous. If  $\Delta S$  is negative, the process in the reverse direction is spontaneous. In the process below

H T T T  $\rightarrow$  T H H T

what is the entropy change? Is the process spontaneous?

A-117  $\Delta S =$  positive. The process is spontaneous. The entropy change can be considered as a driving force tending to place the system in the final state.

Q-118 In the process below

H T T T  $\rightarrow$  T T T T T

what is the entropy change? Is the process spontaneous?

A-118  $\Delta S =$  negative. The process is spontaneous in the reverse direction. In order for the process to occur as written, a force must be applied which overcomes the entropy force. This can be done by adding energy to the system. In such a case,  $\Delta H$  will no longer be zero.

Q-119 Consider the two diagrams below:



(1)

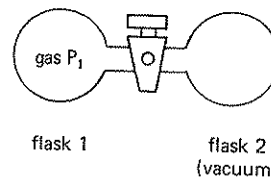


(2)

In diagram (1), a molecule is placed in a box the size of the molecule. In diagram (2) a molecule is placed in a box 9 times as large as box (1). Which system would have the greatest disorder? Why?

A-119 Diagram (2). The molecule has more space in which to move around; therefore, the system would have more disorder. In diagram (1), the molecule is held in a fixed position.

Q-120 The concept of entropy can be applied in the same manner to chemical systems. Consider the expansion of an ideal gas from one container into an evacuated container.



What happens to the gas when the stopcock is opened between the two flasks?

A-120 Gas flows from flask 1 into flask 2 until the pressure in the two flasks is equal.

Q-121 Is there any enthalpy change ( $\Delta H$ ) in the process? Why?

A-121 No.  $\Delta H = 0$ . The only process taking place is that of the molecules moving further apart. Since there are no attractions between ideal gas molecules, no energy is released or absorbed when molecules are moved further apart.

Q-122 Which state has more disorder? Why?

A-122 The final state has more disorder than the initial state. The greater disorder of the final state arises from the molecules having more volume in which to move around.

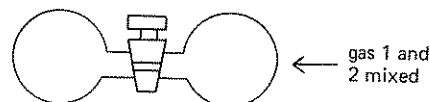
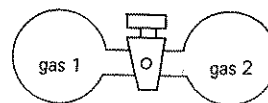
Q-123 The reason the gas expands is that the entropy change for the process is positive. The entropy change is the driving force. Why is the entropy change positive for this process?

A-123 The greater the disorder, the greater is the entropy. Since the disorder in the final state is greater than that of the initial state, the entropy in the final state is greater.

$\Delta S = \text{positive, if } S_{\text{final}} > S_{\text{initial}}$

If the gas had not been ideal, energy would have to be added to break the forces of attraction between the molecules. Therefore, two forces would be at work – an enthalpy force and an entropy force. In this question only the entropy force was considered.

Q-124 Consider the following process for mixing two ideal gases:



Which state (initial or final) has the greater disorder?

A-124 The final state has more disorder. There is more order if the two gases are in their own container.

Q-125 What is the driving force for the above process to take place?

A-125	The change in entropy ( $\Delta S = +$ )	Q-126	Consider the process of dissolving a lump of salt in a beaker of water. What is the sign of the entropy change for this process?
A-126	$\Delta S$ positive. The final state of ions dissolved in $H_2O$ is more disordered than the initial state of the ions in a crystal lattice.	Q-127	Account for the fact that $NH_4NO_3$ dissolves in water even though the enthalpy change is positive.
A-127	When the $NH_4NO_3$ crystal dissolves in $H_2O$ , there is a large positive entropy change. Apparently, the entropy change is a more important factor in this process than the positive enthalpy change.	Q-128	What is the sign for the change in entropy for the freezing of liquid water?
A-128	$\Delta S =$ negative. In the liquid state, water molecules are more disordered than in the ordered solid.	Q-129	Account for the fact that ice melts at $+5^\circ C$ even though the enthalpy change is positive.
A-129	The entropy change for the process is positive. Apparently, the entropy change is more important than the enthalpy change.	Q-130	Which factor, entropy change or enthalpy change, is more important for the spontaneous freezing of water at $-5^\circ C$ ?
A-130	The entropy change would be negative which would tend to make the process go in the opposite direction. Apparently, the negative enthalpy change for the process is more important. Therefore, both factors must be considered in predicting spontaneous processes.	Q-131	What is the sign for the change in entropy for the vaporization of a liquid?
A-131	$\Delta S =$ positive. In the gas state, molecules are less ordered than in the liquid state.	Q-132	Consider the chemical reaction $A + B \rightarrow AB$ What would the sign for the entropy change be for the reaction?
A-132	$\Delta S =$ negative. Since two molecules are combining together to form one molecule, the order of the system is increasing.	Q-133	What would be the sign for the entropy change of this reaction $AB \rightarrow A + B$
A-133	$\Delta S =$ positive. The dissociation reaction causes more disorder in the system.	Q-134	Consider the reaction $A + B \rightarrow C + D$ What would be the sign of the entropy for this reaction?



A-134 If the entropy,  $S$ , of A, B, C, and D is the same,  $\Delta S$  would be zero. This is usually not the case. The entropy of a given molecule depends on the motion of the atoms in the molecule as well as the motion or speed of the molecule itself.

Q-135 Consider two dogs asleep in one kennel and two puppies playing in another kennel. In which kennel will there be the greatest disorder? Why?

A-135 The one containing the puppies will have the greatest disorder because of the greater motion of the animals.

Q-136 How can the motion of a molecule be increased?

A-136 Increasing the temperature.

Q-137 Since disorder is related to motion what must entropy be dependent upon?

A-137 Temperature.

Q-138 As the temperature increases, does the entropy increase or decrease? Why?

A-138 Increase. More motion gives greater disorder.

Q-139 At absolute zero, the entropy of all pure elements and compounds is zero. How can you account for this?

A-139 At absolute zero the kinetic energy is zero and the system is rigid, making it a completely ordered system. A complete lack of disorder results in zero entropy.

Q-140 In order to determine the entropy change for a reaction such as  $A + B \rightarrow C + D$ , the entropy of each compound must be known at the temperature at which the reaction is being carried out. The change in entropy is determined from the relationship

$$\Delta S = \sum nS(\text{products}) - \sum nS(\text{reactants})$$

If the entropies of the reactants and products were

$$S_A^\circ = 83.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S_B^\circ = 105 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S_C^\circ = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S_D^\circ = 96.2 \text{ J mol}^{-1} \text{ K}^{-1}$$

determine the change in entropy for conversion of one mole of A and one mole of B into one mole of C and one mole of D.  $S^\circ$  refers to the entropy at the standard conditions of  $25^\circ \text{C}$  and  $101.3 \text{ kN m}^{-2}$  pressure. (See Table II.)

- A-140 For conversion of one mole of A and one mole of B into one mole of C and one mol of D,

$$\Delta S^\circ = \sum nS_p^\circ - \sum nS_r^\circ$$

$$\Delta S^\circ = [(1 \text{ mol}) (75.3 \text{ J mol}^{-1} \text{ K}^{-1}) + (1 \text{ mol}) (96.2 \text{ J mol}^{-1} \text{ K}^{-1})] - [(1 \text{ mol}) (83.7 \text{ J mol}^{-1} \text{ K}^{-1}) + (1 \text{ mol}) (105 \text{ J mol}^{-1} \text{ K}^{-1})]$$

$$\Delta S^\circ = -17.2 \text{ J K}^{-1}$$

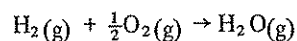
( $\Delta S^\circ$  is the entropy change for the reaction at standard conditions, 101.3 kN m<sup>-2</sup> (1 atm) pressure and 25 °C.)

- Q-141 Provided that the enthalpy change ( $\Delta H$ ) for the above reaction is zero, would the reaction be expected to be spontaneous to the left or right?

A-141  $\Delta S^\circ = -17.2 \text{ J K}^{-1}$

It is spontaneous in the reverse direction or to the left.

- Q-142 What is the entropy change for the reaction



at 25 °C If

$$S_{\text{H}_2}^\circ = 131 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S_{\text{O}_2}^\circ = 205 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S_{\text{H}_2\text{O}}^\circ = 189 \text{ J mol}^{-1} \text{ K}^{-1}$$

- A-142 For the conversion of one mole of H<sub>2</sub> and one half mole of O<sub>2</sub> into one mole of H<sub>2</sub>O,

$$\Delta S^\circ = \sum nS_p^\circ - \sum nS_r^\circ$$

$$\Delta S^\circ = [(1 \text{ mol}) (189 \text{ J mol}^{-1} \text{ K}^{-1})] - [(1 \text{ mol}) (131 \text{ J mol}^{-1} \text{ K}^{-1}) + (\frac{1}{2} \text{ mol}) (205 \text{ J mol}^{-1} \text{ K}^{-1})]$$

$$\Delta S^\circ = -44 \text{ J K}^{-1}$$

The units for this answer would also be J K<sup>-1</sup> per mole of H<sub>2</sub>O formed.

- Q-143 Provided that the enthalpy change ( $\Delta H^\circ$ ) for the above reaction is zero (which it isn't), would the reaction be spontaneous as written?

- A-143 No.  $\Delta S^\circ$  is negative.

- Q-144 Ignoring the effect of  $\Delta H$  on the reaction



and considering only entropy, S, would the reaction be expected to be spontaneous?

$$S^\circ_{\text{CaCO}_3(\text{s})} = 92.9 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^\circ_{\text{CaO}(\text{s})} = 39.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^\circ_{\text{CO}_2(\text{g})} = 214 \text{ J mol}^{-1} \text{ K}^{-1}$$

A-144 For the conversion of one mole of  $\text{CaCO}_3$  into one mole of  $\text{CaO}$  and one mole of  $\text{CO}_2$ ,

$$\Delta S^\circ = \sum n S_p^\circ - \sum n S_r^\circ$$

$$\Delta S^\circ = [(1 \text{ mol}) (39.7 \text{ J mol}^{-1} \text{ K}^{-1}) + (1 \text{ mol}) (214 \text{ J mol}^{-1} \text{ K}^{-1})] - [(1 \text{ mol}) (92.9 \text{ J mol}^{-1} \text{ K}^{-1})]$$

$$\Delta S^\circ = 161 \text{ J K}^{-1}$$

$\Delta S^\circ$  is positive. Therefore, the reaction should be spontaneous.

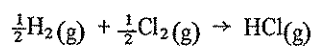
Q-145 Calculate the entropy change which accompanies the formation of 1 mole of gaseous  $\text{HCl}$  from its elements at  $25^\circ\text{C}$ .

$$S_{\text{HCl}}^\circ = 187 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S_{\text{H}_2}^\circ = 131 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S_{\text{Cl}_2}^\circ = 223 \text{ J mol}^{-1} \text{ K}^{-1}$$

A-145 For the conversion of one half mole of  $\text{H}_2$  and one half mole of  $\text{Cl}_2$  into one mole of  $\text{HCl}$ ,



$$\Delta S^\circ = \sum n S_p^\circ - \sum n S_r^\circ$$

$$\Delta S^\circ = [(1 \text{ mole}) (187 \text{ J mol}^{-1} \text{ K}^{-1})] - [(\frac{1}{2} \text{ mole}) (131 \text{ J mol}^{-1} \text{ K}^{-1}) + (\frac{1}{2} \text{ mole}) (223 \text{ J mol}^{-1} \text{ K}^{-1})]$$

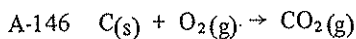
$$\Delta S^\circ = 10 \text{ J K}^{-1}$$

Q-146 Calculate the entropy change which accompanies the formation of 1 mole of gaseous  $\text{CO}_2$  from its elements at  $25^\circ\text{C}$ .

$$S_{\text{CO}_2}^\circ = 214 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S_{\text{C}}^\circ = 158 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S_{\text{O}_2}^\circ = 205 \text{ J mol}^{-1} \text{ K}^{-1}$$

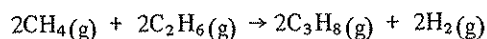


$$\Delta S^\circ = \sum n S^\circ_{\text{p}} - \sum n S^\circ_{\text{r}}$$

$$\Delta S^\circ = [(1 \text{ mol}) (214 \text{ J mol}^{-1} \text{ K}^{-1})] - [(1 \text{ mol}) (158 \text{ J mol}^{-1} \text{ K}^{-1}) + (1 \text{ mol}) (205 \text{ J mol}^{-1} \text{ K}^{-1})]$$

$$\Delta S^\circ = -149 \text{ J K}^{-1}$$

**Q-147** What is the entropy change for the reaction



if  $S^\circ_{\text{CH}_4} = 186 \text{ J mol}^{-1} \text{ K}^{-1}$

$$S^\circ_{\text{C}_2\text{H}_6} = 229 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^\circ_{\text{C}_3\text{H}_8} = 270 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^\circ_{\text{H}_2} = 130 \text{ J mol}^{-1} \text{ K}^{-1}$$

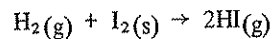
A-147 For the conversion of two moles of  $\text{CH}_4$  and two moles of  $\text{C}_2\text{H}_6$  into two moles of  $\text{C}_3\text{H}_8$  and two moles of  $\text{H}_2$ ,

$$\Delta S^\circ = \sum n S^\circ_{\text{p}} - \sum n S^\circ_{\text{r}}$$

$$\Delta S^\circ = [(2 \text{ mol}) (270 \text{ J mol}^{-1} \text{ K}^{-1}) + (2 \text{ mol}) (130 \text{ J mol}^{-1} \text{ K}^{-1})] - [(2 \text{ mol}) (229 \text{ J mol}^{-1} \text{ K}^{-1}) + (2 \text{ mol}) (186 \text{ J mol}^{-1} \text{ K}^{-1})]$$

$$\Delta S^\circ = -30 \text{ J K}^{-1}$$

**Q-148** The standard entropies for the reactants and products in the reaction



are

$$S^\circ_{\text{H}_2} = 131 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^\circ_{\text{I}_2} = 117 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^\circ_{\text{HI}} = 206 \text{ J mol}^{-1} \text{ K}^{-1}$$

Account for the fact that this reaction is spontaneous even though the enthalpy change was found to be positive.

$$\text{A-148 } \Delta S^\circ = \sum nS_p^\circ - \sum nS_r^\circ$$

$$\Delta S^\circ = [(2 \text{ mol})(206 \text{ J mol}^{-1} \text{ K}^{-1})] - [(1 \text{ mol})(131 \text{ J mol}^{-1} \text{ K}^{-1}) + (1 \text{ mol})(117 \text{ J mol}^{-1} \text{ K}^{-1})]$$

$$\Delta S^\circ = 164 \text{ J K}^{-1}$$

The reaction has a positive entropy. Apparently this is more important than the endothermic nature of the reaction. This again points out the importance of considering both enthalpy and entropy changes.

- R
- a) The greater the disorder, the greater is the probability.
  - b) The greater the probability, the greater is the entropy.
  - c)  $S^\circ$  = standard entropy (25 °C and 1 atm or 101.3 kN m<sup>-2</sup> pressure).
  - d)  $\Delta S^\circ = \sum nS_p^\circ - \sum nS_r^\circ$
  - e) For a constant pressure process and one in which there is no enthalpy change,
    - $\Delta S^\circ$  = positive (spontaneous change)
    - $\Delta S^\circ$  = negative (spontaneous in reverse direction)
  - f) When the enthalpy change is not zero, both enthalpy and entropy changes must be considered in determining whether a process is spontaneous.

- S-10 Which of the two factors, enthalpy or entropy change, will determine the direction of a spontaneous reaction or process if they are opposed to each other, i.e.,  $\Delta S = +$ ,  $\Delta H = +$  or  $\Delta S = -$ ,  $\Delta H = -$ ? To answer this question a new function,  $G$ , is introduced which includes both the enthalpy factor and the entropy factor. The new function is called free energy and is defined at constant pressure by the expression

$$\Delta G = \Delta H - T\Delta S \quad \text{where } \Delta G = \sum nG(\text{products}) - \sum nG(\text{reactants})$$

The  $\Delta H$  term is a measure of the total change in energy for the reaction or process and the  $T\Delta S$  term is a measure of the change in energy which results from the rearrangement of atoms during the reaction or process. Therefore, free energy change is a measure of the energy available to do work which accounts for its name.

- Q-149 From the expression for  $\Delta G$  in terms of  $\Delta H$  and  $\Delta S$  and a knowledge that if  $\Delta H = 0$ ,  $\Delta S$  is a measure of the spontaneity of a reaction, what should the sign of  $\Delta G$  be for a spontaneous process and what should it be for a non-spontaneous process?

A-149  $\Delta G = \Delta H - T\Delta S$

$\Delta H = 0$

When  $\Delta S$  is positive the reaction is spontaneous.

Therefore,  $\Delta G$  is negative for a spontaneous reaction.

When  $\Delta S$  is negative the reaction is non-spontaneous.

Therefore,  $\Delta G$  is positive for a non-spontaneous reaction.

Q-150 It is now possible to determine the spontaneity of any chemical process regardless of whether or not the enthalpy change is zero. To determine the spontaneity of a reaction the enthalpies and entropies of both products and reactants at the same temperature, i.e., standard state, must be known.

Calculate the change in free energy,  $\Delta G$ , for the following reaction at 25 °C. Remember T must be used as absolute temperature.



	$\Delta H^\circ_f / \text{kJ mol}^{-1}$	$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$
$\text{H}_2$	0	131
$\text{O}_2$	0	205
$\text{H}_2\text{O}$	-242	189

These values were obtained from Table I and Table II (p. 375 and 376).

Is the reaction spontaneous?

A-150 For the conversion of one mole of  $\text{H}_2$  and one half mole of  $\text{O}_2$  into one mole of  $\text{H}_2\text{O}$ ,

$$\Delta H^\circ = \sum n\Delta H^\circ_f(\text{p}) - \sum n\Delta H^\circ_f(\text{r})$$

$$\Delta H^\circ = [(1 \text{ mole})(242 \text{ kJ mol}^{-1})] - [0 + 0]$$

$$\Delta H^\circ = -242 \text{ kJ}$$

$$\Delta S^\circ = \sum nS^\circ_{\text{p}} - \sum nS^\circ_{\text{r}}$$

$$\Delta S^\circ = [(1 \text{ mol})(189 \text{ J mol}^{-1} \text{K}^{-1})] - [(1 \text{ mol})(131 \text{ J mol}^{-1} \text{K}^{-1}) + (\frac{1}{2} \text{ mol})(205 \text{ J mol}^{-1} \text{K}^{-1})]$$

$$\Delta S^\circ = -44 \text{ J K}^{-1}$$

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

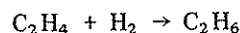
$$\Delta G^\circ = -242 \text{ kJ} - (298)(-44.5 \text{ J K}^{-1}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$$\Delta G^\circ = -242 \text{ kJ} + 13.3 \text{ kJ}$$

$$\Delta G^\circ = -228 \text{ kJ}$$

It is spontaneous.  $\Delta G^\circ$  is the free energy change for the reaction at standard conditions, 101.3 kN m<sup>-2</sup> (1 atm) pressure and 25 °C.

Q-151 Calculate the change in free energy ( $\Delta G^\circ$ ) at 25 °C for the following chemical reaction



Is the reaction spontaneous?

Obtain information needed from Table I and Table II.

A-151 From Table I and II

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$
$\text{C}_2\text{H}_4$	52.3	219
$\text{H}_2$	0	131
$\text{C}_2\text{H}_6$	-84.7	229

$$\Delta H^\circ = [(1 \text{ mol}) (-84.7 \text{ kJ mol}^{-1})] - [(1 \text{ mol}) (52.3 \text{ kJ mol}^{-1}) + 0]$$

$$\Delta H^\circ = -137 \text{ kJ}$$

$$\Delta S^\circ = [(1 \text{ mol}) (229 \text{ J mol}^{-1} \text{K}^{-1})] - [(1 \text{ mol}) (131 \text{ J mol}^{-1} \text{K}^{-1}) + (1 \text{ mol}) (219 \text{ J mol}^{-1} \text{K}^{-1})]$$

$$\Delta S^\circ = -121 \text{ J K}^{-1}$$

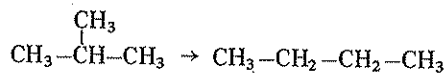
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -137 - \frac{(298)(-121)}{1000}$$

$$\Delta G^\circ = -137 + 36 = -101 \text{ kJ}$$

Spontaneous.

Q-152 Calculate the change in free energy at 25 °C for the isomerization of isobutane into n-butane.



isobutane

n-butane

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$
isobutane	-132	295
n-butane	-125	310

A-152 
$$\Delta H^\circ = [(1 \text{ mol}) (-125 \text{ kJ mol}^{-1})] - [(1 \text{ mol}) (-132 \text{ kJ mol}^{-1})]$$

$$\Delta H^\circ = 7 \text{ kJ}$$

$$\Delta S^\circ = [(1 \text{ mol}) (310 \text{ J mol}^{-1} \text{K}^{-1})] - [(1 \text{ mol}) (295 \text{ J mol}^{-1} \text{K}^{-1})]$$

$$\Delta S^\circ = 15 \text{ J K}^{-1}$$

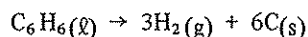
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 7 - \frac{(298)(15)}{1000}$$

$$\Delta G^\circ = 7 - 4.5 = 2.5 \text{ kJ}$$

Spontaneous in reverse direction.Q-153 Calculate the change in free energy for the decomposition of benzene ( $\text{C}_6\text{H}_6(\ell)$ ) into its elements at 25 °C.

A-153 (From Table I and II)

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$
Benzene	49.0	173
$\text{H}_2$	0	131
C	0	5.73



$$\Delta H^\circ = [0 + 0] - [(1 \text{ mol}) (49.0 \text{ kJ mol}^{-1})]$$

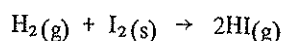
$$\Delta H^\circ = -49.0 \text{ kJ}$$

$$\Delta S^\circ = [(3 \text{ mol}) (131 \text{ J mol}^{-1} \text{K}^{-1}) + (6 \text{ mol}) (5.73 \text{ J mol}^{-1} \text{K}^{-1})] - [(1 \text{ mol}) (173 \text{ J mol}^{-1} \text{K}^{-1})]$$

$$\Delta S^\circ = 254 \text{ J K}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -49.0 - \frac{(298)(254)}{1000}$$

$$\Delta G^\circ = -49.0 - 75.7 = -125 \text{ kJ}$$

Spontaneous.Q-154 Calculate the change in free energy at  $50^\circ\text{C}$  for the following chemical reaction.

Is the reaction spontaneous?

Obtain information needed from Table I and Table II and assume that  $\Delta H$  and  $\Delta S$  are the same at  $50^\circ\text{C}$  as they are at  $25^\circ\text{C}$ .

A-154 From Tables I and II

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
$\text{H}_2(\text{g})$	0.0	131
$\text{I}_2(\text{s})$	0.0	117
$\text{HI}(\text{g})$	25.9	206

$$\Delta H^\circ = [(2 \text{ mol}) (25.9 \text{ kJ mol}^{-1})] - [(1 \text{ mol}) (0.0) + (1 \text{ mol}) (0.0)]$$

$$\Delta H^\circ = 51.8 \text{ kJ}$$

$$\Delta S^\circ = [(2 \text{ mol}) (206 \text{ J K}^{-1} \text{mol}^{-1})] - [(1 \text{ mol}) (117 \text{ J mol}^{-1} \text{K}^{-1}) + (1 \text{ mol}) (131 \text{ J mol}^{-1} \text{K}^{-1})]$$

$$\Delta S^\circ = 164 \text{ J K}^{-1}$$

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

$$T = 273 + 50 = 323$$

$$= 51.2 - \frac{(323)(164)}{1000}$$

$$= 51.2 - 53.0$$

$$\Delta G = -1.8 \text{ kJ}$$

Spontaneous

Q-155 If the temperature is lowered and assuming that  $\Delta H$  and  $\Delta S$  do not vary with temperature, what happens to the value of  $\Delta G$ ?

A-155 It will increase.

Q-156 Can the value of  $\Delta G$  from A-154 ever reverse sign? When?



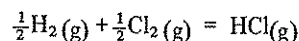
A-156 Yes. When the temperature becomes so low that the  $\Delta H$  term is more negative than the  $T\Delta S$  term ( $37^\circ\text{C}$ ).

Q-157 If enthalpy and entropy changes are opposing each other, under what conditions will the enthalpy term be more important and when will the entropy term be more important?

A-157 The enthalpy term will be more important at low temperatures and the entropy term the more important at high temperatures.

Q-158 Just as standard enthalpy and entropy values were given for compounds, standard free energy of formation values are given (Table III). The standard free energy of formation,  $\Delta G_f^\circ$ , for a compound is the change in free energy which accompanies the formation of one mole of the compound from its pure elements. The free energy of formation of an element in its standard state is assigned a value of zero by convention.

What is the free energy change for the reaction



if  $G_{\text{HCl}}^\circ = -95.4 \text{ kJ mol}^{-1}$ ?

$$\begin{aligned}\text{A-158 } \Delta G^\circ &= \sum n G_p^\circ - \sum n G_r^\circ \\ \Delta G^\circ &= [(1 \text{ mol})(-95.4 \text{ kJ mol}^{-1})] - [0 + 0] \\ \Delta G^\circ &= -95.4 \text{ kJ mol}^{-1}\end{aligned}$$

Q-159 What is the standard free energy of formation for  $\text{HCl}(\text{g})$ ?

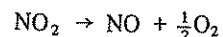
A-159 Conversion of one-half mole of  $\text{H}_2$  and one-half mole of  $\text{Cl}_2$  into one mole of  $\text{HCl}$  is obtained from A-158.  $\Delta G^\circ$  for the reaction is  $-95.4 \text{ kJ}$ . From the definition for standard free energy of formation,

$$\frac{\Delta G^\circ}{(1 \text{ mole})} = \Delta G_f^\circ(\text{HCl}) = -95.4 \text{ kJ mol}^{-1}$$

Q-160 What is the relationship between free energy of a compound,  $G^\circ$ , and the standard free energy of formation for the compound,  $\Delta G_f^\circ$ ?

A-160 Identical  
 $G_{\text{AB}}^\circ = \Delta G_f^\circ(\text{AB})$

Q-161 Calculate the free energy change for the reaction



at  $25^\circ\text{C}$  from the standard free energies of formation.

$$\Delta G_f^\circ(\text{NO}_2) = 51.9 \text{ kJ mol}^{-1}$$

$$\Delta G_f^\circ(\text{NO}) = 86.6 \text{ kJ mol}^{-1}$$

A-161  $\Delta G^\circ = \sum n\Delta G_f^\circ(p) - \sum n\Delta G_f^\circ(r)$

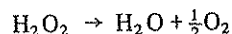
$$\Delta G^\circ = [0 + (1 \text{ mol})(86.6 \text{ kJ mol}^{-1})] - [(1 \text{ mol})(51.9 \text{ kJ mol}^{-1})]$$

$$\Delta G^\circ = 34.7 \text{ kJ}$$

Spontaneous in reverse direction.

Q-162 Calculate the standard free energy of formation for  $\text{H}_2\text{O}_2$ .

The free energy change for the reaction



is  $\Delta G^\circ = -125 \text{ kJ mol}^{-1}$

and  $\Delta G_f^\circ(\text{H}_2\text{O}) = -228 \text{ kJ mol}^{-1}$

A-162  $\Delta G^\circ = \sum n\Delta G_f^\circ(p) - \sum n\Delta G_f^\circ(r)$

$$-125 \text{ kJ} = [0 + (1 \text{ mol})(-228 \text{ kJ mol}^{-1})] - [(1 \text{ mol})(\Delta G_f^\circ(\text{H}_2\text{O}_2))]$$

$$\Delta G_f^\circ(\text{H}_2\text{O}_2) = -103 \text{ kJ mol}^{-1}$$

**Q-163** The heat of vaporization ( $\Delta H$ ) of water at  $105^\circ$  is  $40.1 \text{ kJ mol}^{-1}$ . The entropy change is  $108 \text{ J mol}^{-1} \text{ K}^{-1}$ . What is the free energy change for the conversion of one mole of liquid water at  $105^\circ\text{C}$  into steam?

A-163  $\Delta G = \Delta H - T\Delta S$

$$\Delta G = 40.1 \text{ kJ} - \frac{(378)(108)}{1000} \text{ kJ}$$

$$\Delta G = 40.1 - 40.8 = -0.7 \text{ kJ mol}^{-1}$$

Spontaneous

**Q-164** If the values for  $\Delta H$  and  $\Delta S$  were the same for the vaporization of  $\text{H}_2\text{O}$  at  $90^\circ\text{C}$  as they were at  $105^\circ\text{C}$ , what would be the value for the change in free energy for the conversion of one mole of water into vapor at  $90^\circ\text{C}$ ?

A-164  $\Delta G = \Delta H - T\Delta S$

$$\Delta G = 40.1 \text{ kJ} - \frac{(363)(108)}{1000} \text{ kJ}$$

$$\Delta G = 40.1 - 39.2 = 0.9 \text{ kJ mol}^{-1}$$

Not spontaneous

This illustrates the effect of temperature in the entropy term.

**Q-165** At equilibrium, the reaction or process can go in either direction. The entropy term ( $T\Delta S$ ) and enthalpy term ( $\Delta H$ ) balance each other out. What would be the value of  $\Delta G$  at equilibrium? At what temperature would this occur for  $\text{H}_2\text{O}$  vaporization at  $101.3 \text{ kN m}^{-2}$ ?

A-165  $T\Delta S = \Delta H$

$$\Delta G = 0$$

$$40.1 \text{ kJ} = T(0.108 \text{ kJ K}^{-1})$$

$$T = 374 \text{ K or } 101^\circ\text{C}$$

$$(\text{Experimental value} = 100^\circ\text{C})$$

**Q-166** At what temperature will the entropy ( $T\Delta S$ ) term balance out the enthalpy term ( $\Delta H$ ) in the ice-water system?