

CHM 3400 – Fundamentals of Physical Chemistry
Chapter 2 - Handout

1. Basic concepts and the first law

Thermodynamics is the study of energy transformations and associated processes in systems. A system is a part of the Universe that scientists have selected for detailed study. Systems can be open (exchanging both mass and energy with the surroundings), closed (exchanging energy, but not mass) or isolated (no exchange of either mass or energy with the surroundings).

Thermodynamics involves various quantities such as work, heat, internal energy, enthalpy, and so forth. Some of these are state functions. A state function is a function whose change in value depends only on the initial and final state of the system, that is, its change in value is independent of the path used to move from the initial to final state. Alternatively, one can define a state function as a function whose change in value for any closed path (a path where the initial and final state are the same) is equal to zero. Internal energy and enthalpy (discussed below) are examples of state functions. Some thermodynamic quantities, such as work and heat, are not state functions (and in fact are not really functions at all). The distinction between state functions and things that are not state functions is important, as will become clear.

Thermodynamics is governed by general principles, called the laws of thermodynamics. One of these, the first law, is a relationship involving work, heat, and internal energy.

Work (w) can be defined as

$$\delta w = F \cdot dx \qquad w = \int_i^f \delta w = \int_i^f F \cdot dx \qquad (2.1.1)$$

In the above expressions F and dx are vectors, and δw represents a small amount of work. The symbol " δ " is used as a reminder that work is not a state function (technically, it means that δw is not an exact differential). For the integrals, i indicates the initial state and f the final state of the system.

There are several different types of work that systems can carry out. For now we will focus on mechanical work (sometimes called pressure-volume work), the work associated with the change in the volume of a system. Starting with eq 2.1.1, we can show that for a system expanding against an external pressure p_{ex} , the work that occurs is

$$\delta w = - p_{\text{ex}} dV \qquad w = - \int_i^f p_{\text{ex}} dV \qquad (2.1.2)$$

where dV represents the change in the volume of the system. Note that eq 2.1.2 means that when a system expands work is negative (the system is doing work on the surroundings), while when a system is compressed work is positive (work is done on the system by the surroundings).

Heat (q), sometimes called thermal energy, is the energy exchanged by two systems initially at equilibrium at different temperatures when they are placed in contact with one other (Fig 1 on the next page). Heat is the energy that moves from the warmer system (initially at temperature T_1) to the cooler system (initially at temperature T_2) until a uniform final temperature T_3 is reached (with $T_1 > T_3 > T_2$). By convention, positive heat ($q > 0$) corresponds to heat entering a system from its surroundings, defined as an endothermic process. Negative heat ($q < 0$) corresponds to heat moving from the system to its surroundings, defined as an exothermic process. Like work, heat is not a state function.

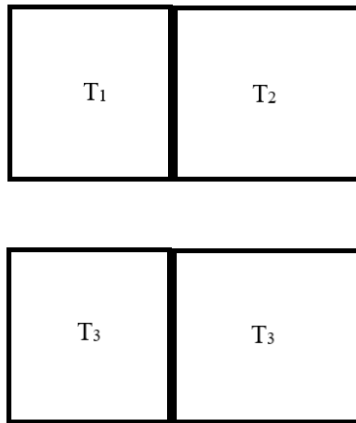


Figure 1. Two object initially at equilibrium at different temperatures, with $T_1 > T_2$. When placed in contact, heat will move between the warm system and the cool system until equilibrium is reestablished at an intermediate temperature T_3 .

Internal energy (U) is the total amount of energy possessed by a system, including kinetic energy and various forms of potential energy (gravitational, chemical, electrical, and so forth). While it is difficult to account for all of the different forms of energy a system possesses, in thermodynamics we are only concerned with changes in internal energy (dU for a small change, ΔU for a large change). Unlike work and heat, internal energy is a state function.

The first law of thermodynamics is the statement

$$dU = dq + dw \qquad \Delta U = q + w \qquad (2.1.3)$$

The first law is equivalent to conservation of energy, believed to be a general property of the Universe.

We will often discuss various types of processes that can be carried out on systems. These can be divided into two general categories. A reversible process is a process that takes place through a large number of small individual steps. For a reversible process where the only work taking place is mechanical work it will always be the case that $p_{\text{ex}} = p$, where p is the pressure of the system. An irreversible process has at least one step that is not reversible (and so at least one step where $p_{\text{ex}} \neq p$).

There are other ways of classifying processes.

isothermal ($T = \text{constant}$)

isobaric ($p = \text{constant}$)

isochoric ($V = \text{constant}$)

adiabatic ($q = 0$)

Finally, since we often use systems containing an ideal gas as examples of thermodynamic processes, it is useful to know that the internal energy of an ideal gas (unlike other substances) depends only on temperature.

As an example of the use of the first law of thermodynamics, consider the isothermal expansion of 1.000 mole of an ideal gas from an initial pressure $p_i = 4.000$ atm to a final pressure $p_f = 2.000$ atm, at $T = 300.0$ K. We will consider two ways of carrying out the expansion:

1) An isothermal irreversible expansion (against a constant external pressure $p_{\text{ex}} = p_f = 2.000 \text{ atm}$).

Since the process is isothermal and the energy of an ideal gas only depends on temperature, $\Delta U = 0$. From the first law, $\Delta U = q + w$, and so $q = -w$. To find w , we use eq 2.1.2

$$w = - \int_i^f p_{\text{ex}} dV = - p_{\text{ex}} \int_i^f dV = - p_f (V_f - V_i) \quad (2.1.4)$$

where we have made use of the fact that the expansion is against a constant external pressure, which allows p_{ex} to be taken outside of the integral. Using the ideal gas law, $V_i = 6.16 \text{ L}$, $V_f = 12.32 \text{ L}$, and so

$$w = - (2.000 \text{ atm}) (12.32 \text{ L} - 6.16 \text{ L}) = - 12.32 \text{ L} \cdot \text{atm} (101.3 \text{ J/L} \cdot \text{atm}) = - 1247 \text{ J}$$

$$q = - w = + 1247 \text{ J}$$

2) An isothermal reversible expansion

As with the isothermal irreversible expansion, $\Delta U = 0$, and so $q = -w$. Since the expansion is reversible, $p_{\text{ex}} = p = nRT/V$, and so

$$w = - \int_i^f p_{\text{ex}} dV = - \int_i^f p dV = - \int_i^f (nRT/V) dV = - nRT \ln(V_f/V_i) \quad (2.1.5)$$

Using the values for V_i and V_f obtained for the isothermal irreversible expansion, we get

$$w = - (1.000 \text{ mol}) (8.3145 \text{ J/mol} \cdot \text{K}) (300.0 \text{ K}) \ln[(12.32 \text{ L})/(6.16 \text{ L})] = - 1729 \text{ J}$$

$$q = -w = + 1729 \text{ J}$$

Note that while q and w are different for the two processes, ΔU is the same, consistent with the idea that work and heat are not state functions, but internal energy is a state function.

2. Partial derivatives and partial derivative relationships

For $f(x)$, a function of one variable, the rate of change of the function can be written as

$$df = (df/dx) dx \quad (2.2.1)$$

where (df/dx) is the derivative of the function, found using standard techniques from calculus.

By analogy with the above the rate of change of a function of two variables, $f(x,y)$, can be written as

$$df = (\partial f/\partial x)_y dx + (\partial f/\partial y)_x dy \quad (2.2.2)$$

where $(\partial f/\partial x)_y$ and $(\partial f/\partial y)_x$ are the partial derivatives of the function f with respect to x and with respect to y . Note that we use $\partial f/\partial x$ to indicate a partial derivative, and list the independent variables being held constant outside of the parentheses enclosing the partial derivative. Equation 2.2.2 can be generalized in a straightforward manner to functions of more than two variables.

The partial derivative of a function is found by treating all variables except the one for which the partial derivative is being taken as if they are constants. Thus, finding the partial derivative of a function of several variables is no more difficult than finding the normal derivative of a function of one variable.

EXAMPLE: If $f(x,y) = 4x^3 + 2xy^2 + 7y + 1$, then: $(\partial f/\partial x)_y = 12x^2 + 2y^2$ $(\partial f/\partial y)_x = 4xy + 7$

3. Heat capacity and enthalpy

The heat capacity for a substance is defined as the ratio of the heat added divided by the temperature change.

$$C = \delta q/dT \cong q/\Delta T \quad (2.3.1)$$

Note that heat capacity as defined above is not a state function, since δq is a path dependent quantity.

There are ways in which the above definition of heat capacity can be made more specific. In particular, we define the constant volume and constant pressure heat capacities as

$$C_V = (\delta q/dT)_V \quad C_p = (\delta q/dT)_p \quad (2.3.2)$$

where the subscripts "V" and "p" indicate that we are limiting ourselves to constant volume or constant pressure processes, respectively.

From the first law of thermodynamics

$$dU = \delta q + \delta w \quad (2.3.3)$$

From the definition of mechanical ("pressure-volume") work

$$\delta w = - p_{ex} dV \quad (2.3.4)$$

It is clear from eq 2.3.4 that $\delta w = 0$ for a constant volume processes. Therefore $dU = \delta q_V$ (where the subscript "V" is to remind us that this relationship is true only for constant volume processes). If we integrate both sides of this relationship for a process carried out at constant volume it follows that for such a process $q_V = \Delta U$, where the subscript "V" is again a reminder that this is true only if volume is kept constant. If we substitute into the expression for C_V (eq 2.3.2), we get

$$C_V = (\delta q/dT)_V = (dU/dT)_V = (\partial U/\partial T)_V \quad (2.3.5)$$

The importance of eq 2.3.5 is that it gives C_V in terms of a partial derivative of a state function. C_V is therefore a state function.

To find an analogous expression that applies to constant pressure processes, we begin by defining a new thermodynamic function, enthalpy

$$H = U + pV \quad (2.3.6)$$

Note that since U , p , and V are state functions H is also a state function. For a small change in H , we have

$$dH = dU + d(pV) = dU + p dV + V dp \quad (2.3.7)$$

If we use the first law (eq 2.1.3) to substitute for dU , and limit ourselves to reversible processes (where $p_{ex} = p$, and so where $\delta w = - p_{ex}dV = - p dV$), then

$$dH = \delta q + \delta w + p dV + V dp = \delta q - p dV + p dV + V dp = \delta q + V dp \quad (2.3.8)$$

However, because enthalpy is a state function, it follows that since eq 2.3.8 is true for reversible processes it is true for any process.

Now consider a constant pressure process. For such a process $dp = 0$. Therefore

$$dH = \delta q_p \quad (2.3.9)$$

(where the subscript "p" reminds us the above relationship is limited to constant pressure processes). Note that it follows from eq 2.3.9 that for constant pressure processes $q_p = \Delta H$. This is the significance of enthalpy - the change in enthalpy is equal to q for a constant pressure process.

If we use eq 2.3.9 to substitute into the defining equation for C_p (eq 2.3.2), then

$$C_p = (\delta q/dT)_p = (dH/dT)_p = (\partial H/\partial T)_p \quad (2.3.10)$$

As was the case with C_v , the above relationship gives C_p in terms of the partial derivative of a state function, and therefore means that C_p is a state function.

There are a number of general relationships that can now be found. For example, if we write $U = U(V,T)$ and $H = H(p,T)$ (that is, express internal energy and enthalpy as functions of two variables), then

$$dU = (\partial U/\partial V)_T dV + (\partial U/\partial T)_V dT = (\partial U/\partial V)_T dV + C_v dT \quad (2.3.11)$$

$$dH = (\partial H/\partial p)_T dp + (\partial H/\partial T)_p dT = (\partial H/\partial p)_T dp + C_p dT \quad (2.3.12)$$

Equations 2.3.11 and 2.3.12 are true in general. Two additional relationships follow from the above. For constant volume processes

$$dU = C_v dT \quad \Delta U = \int_i^f C_v dT \quad (\text{all constant volume processes}) \quad (2.3.13)$$

while for constant pressure processes

$$dH = C_p dT \quad \Delta H = \int_i^f C_p dT \quad (\text{all constant pressure processes}) \quad (2.3.14)$$

There are also two general statements we can make for processes involving ideal gases. Since for an ideal gas U and H are functions only of temperature, it follows that $(\partial U/\partial V)_T = 0$ and $(\partial H/\partial p)_T = 0$. Therefore (from eq 2.3.11, 2.3.12, 2.3.13, and 2.3.14)

$$\Delta U = \int_i^f C_v dT \quad \Delta H = \int_i^f C_p dT \quad (\text{all processes on ideal gases}) \quad (2.3.15)$$

It is important to keep in mind that eq 2.3.13, 2.3.14, and 2.3.15 are not true in general, but only for the restricted sets of processes indicated with each set of equations. Nevertheless, these equations are often useful in thermodynamic calculations.

To summarize:

Finding ΔU Equation 2.3.11 is true in general.
 Equation 2.3.13 applies to all processes carried out at constant volume.
 Equation 2.3.15 applies to all ideal gas processes, even if the process is not constant volume.

Finding ΔH Equation 2.3.12 is true in general.
 Equation 2.3.14 applies to all processes carried out at constant pressure.
 Equation 2.3.15 applies to all ideal gas processes, even if the process is not constant pressure.

Finally, there is a useful relationship between C_p and C_v for an ideal gas (which can be derived)

$$C_p - C_v = nR \quad (\text{ideal gases only}) \quad (2.3.16)$$

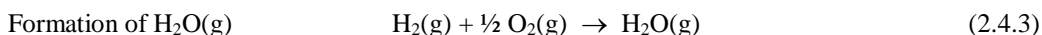
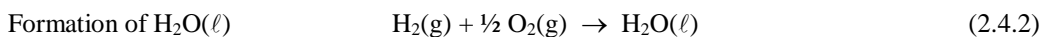
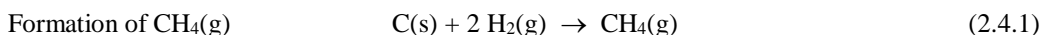
If we define the molar heat capacities (heat capacity per mole of substance) as $C_{v,m} = C_v/n$ and $C_{p,m} = C_p/n$, then dividing both sides of eq 2.3.16 by n gives the result

$$C_{p,m} - C_{v,m} = R \quad (\text{ideal gases only}) \quad (2.3.17)$$

4. Enthalpy change for a chemical reaction

Because it is far more common for chemists to work under conditions of constant pressure than conditions of constant volume, there is generally more use of enthalpy in thermochemistry than internal energy. Several applications of the concepts from the previous sections to systems of interest are given below.

Before proceeding, it is useful to discuss formation reactions. By definition, the formation reaction for a substance is the reaction that produces exactly one mole of the substance (in its specified state) from elements in their standard state (thermodynamically most stable state, taken as $p = 1.000$ bar, and most commonly $T = 25.0$ °C), with no other reactants or products. The following are examples of formation reactions:



While we normally use the smallest set of whole number coefficients to balance a chemical reaction, we do not do this with formation reactions. This is because of the requirements in the definition of the formation reaction.

If we carry out one mole of a formation reaction (for example, react one mole of solid carbon with two moles of hydrogen gas to form one mole of methane, as in eq 2.4.1) under conditions of constant pressure, and with $T_i = T_f$, then it follows that $q_p = \Delta H$. Since q is something that can be measured experimentally, this gives a practical method for finding ΔH° for this and other chemical reactions. Note that when we have a formation reaction carried out for standard conditions (with all reactant present in the system, 1.000 bar pressure for gases, 1.00 M concentration for solutes, and assuming ideal behavior) and standard temperature (usually taken to be 25.0 °C) we use the symbol ΔH°_f to represent the change in enthalpy. So, for example, we would represent the value for the enthalpy of formation for methane gas as $\Delta H^\circ_f(\text{CH}_4(\text{g}))$.

For an arbitrary chemical reaction we call the change of enthalpy for standard conditions $\Delta H^\circ_{\text{rxn}}$. For example, for the reaction



the change of enthalpy for the process for standard conditions is $\Delta H^\circ_{\text{rxn}}$.

There is a useful relationship between $\Delta H^\circ_{\text{rxn}}$ for a chemical reaction and the formation enthalpies of the reactants and products. Consider the following combination of reactions:



Since the combination of the three reactions above the line (2.4.6, 2.4.7, and 2.4.8) add up to the reaction below the line (2.4.9), and since enthalpy is a state function, it follows that

$$\Delta \text{H}^\circ_{\text{rxn}} = 3 \Delta \text{H}^\circ_{\text{f}}(\text{NO}(\text{g})) - [\Delta \text{H}^\circ_{\text{f}}(\text{NO}_2(\text{g})) + \Delta \text{H}^\circ_{\text{f}}(\text{N}_2\text{O}(\text{g}))] \quad (2.4.10)$$

Using the same procedure for any reaction gives the following relationship for $\Delta \text{H}^\circ_{\text{rxn}}$ in terms of the enthalpies of formation of the reactants and products:

$$\Delta \text{H}^\circ_{\text{rxn}} = [\sum \Delta \text{H}^\circ_{\text{f}}(\text{products})] - [\sum \Delta \text{H}^\circ_{\text{f}}(\text{reactants})] \quad (2.4.11)$$

where the summation includes all of the products or all of the reactants. In using eq 2.4.11 we must take into account the coefficients used to balance the reaction, as was done in the example.

Equation 2.4.11 is a powerful result. It means that if we have values for the formation enthalpies for all of the reactants and products for a chemical reaction at a particular temperature we can find the value for $\Delta \text{H}^\circ_{\text{rxn}}$ at that temperature. We can do this even for reactions that we have not carried out in the lab. These data, along with other useful data, are compiled in thermochemical tables like the one in the Appendix of the text (usually for $T = 25.0 \text{ }^\circ\text{C}$).

An equation for finding the change in enthalpy for a constant pressure process at any temperature can also be found. The result (not derived) is

$$\Delta \text{H}^\circ_{\text{rxn}}(T_2) = \Delta \text{H}^\circ_{\text{rxn}}(T_1) + \int_{T_1}^{T_2} \Delta C_{\text{p,m}} dT \quad (2.4.12)$$

where

$$\Delta C_{\text{p,m}} = [\sum C_{\text{p,m}}(\text{products})] - [\sum C_{\text{p,m}}(\text{reactants})] \quad (2.4.13)$$

For example, for the reaction in 2.4.5

$$\Delta C_{\text{p,m}} = [3 C_{\text{p,m}}(\text{NO}(\text{g}))] - [C_{\text{p,m}}(\text{NO}_2(\text{g})) + C_{\text{p,m}}(\text{N}_2\text{O}(\text{g}))] \quad (2.4.14)$$

If we know the value for $\Delta \text{H}^\circ_{\text{rxn}}$ at a temperature T_1 , and have sufficient information to find $\Delta C_{\text{p,m}}$, we can use eq 2.4.12 to find $\Delta \text{H}^\circ_{\text{rxn}}$ at a temperature T_2 .

Equation 2.4.12 takes a particularly simple form if we can assume that the constant pressure molar heat capacities for the products and reactants are all independent of temperature. In that case, $\Delta C_{\text{p,m}}$ has a constant value, and so

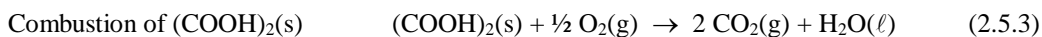
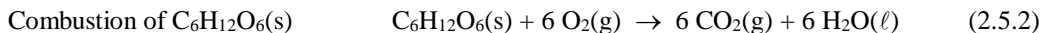
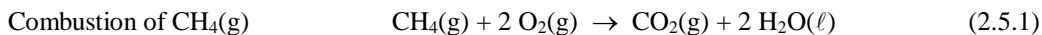
$$\Delta \text{H}^\circ_{\text{rxn}}(T_2) \cong \Delta \text{H}^\circ_{\text{rxn}}(T_1) + \Delta C_{\text{p,m}} (T_2 - T_1) \quad (2.4.15)$$

This is often a reasonable assumption, particularly when T_1 and T_2 are close in value.

5. Enthalpy changes for other processes

Combustion

Like the formation reaction, the combustion reaction has a specific definition. The combustion reaction is defined as the reaction of one mole of a single substance with oxygen to form combustion products. For compounds containing only carbon, hydrogen, and oxygen the combustion products are $\text{CO}_2(\text{g})$ (for carbon) and $\text{H}_2\text{O}(\ell)$ (for hydrogen). For example, the combustion reactions for methane, glucose, and oxalic acid are:



As is the case with formation reactions, combustion reactions must satisfy the specific definition given above, which sometimes leads to a balanced reaction with a fractional stoichiometric coefficient.

The enthalpy of combustion for a substance is defined as the change in enthalpy when one mole of the substance undergoes combustion under conditions of constant pressure and temperature. For standard pressure, the symbol $\Delta H^\circ_{\text{comb}}$ is used to represent the change in enthalpy for one mole of the combustion reaction. So, for example, we would represent the value for the enthalpy of combustion for methane gas as $\Delta H^\circ_{\text{comb}}(\text{CH}_4(\text{g}))$.

Because combustion reactions, when carried out under conditions of excess oxygen, generally do not form products other than combustion products, such reactions are useful in finding formation enthalpies for organic compounds. For example, for the reaction in eq 2.5.3, the enthalpy of combustion is given by the expression

$$\begin{aligned} \Delta H^\circ_{\text{comb}}((\text{COOH})_2(\text{s})) = [& 2 \Delta H^\circ_{\text{f}}(\text{CO}_2(\text{g})) + \Delta H^\circ_{\text{f}}(\text{H}_2\text{O}(\ell))] \\ & - [\Delta H^\circ_{\text{f}}((\text{COOH})_2(\text{s})) + \frac{1}{2} \Delta H^\circ_{\text{f}}(\text{O}_2(\text{g}))] \quad (2.5.4) \end{aligned}$$

Since there are accurate values for $\Delta H^\circ_{\text{f}}(\text{CO}_2(\text{g}))$ and $\Delta H^\circ_{\text{f}}(\text{H}_2\text{O}(\ell))$, and since $\Delta H^\circ_{\text{f}}(\text{O}_2(\text{g}))$ is equal to zero, everything on the right side of eq 2.5.4 is known except the value for $\Delta H^\circ_{\text{f}}((\text{COOH})_2(\text{s}))$. Therefore, by measuring the enthalpy of combustion for oxalic acid (by bomb calorimetry, for example), the enthalpy of formation can be found.

Since bomb calorimetry, the most common technique used to study combustion reactions, is a constant volume process, it is the energy of combustion ($\Delta U^\circ_{\text{comb}}$) that is experimentally found. This can be used to find the corresponding value for the enthalpy of combustion. Since

$$H = U + pV \quad (2.5.5)$$

it follows that

$$\Delta H_{\text{comb}} = \Delta U_{\text{comb}} + \Delta(pV) \quad (2.5.6)$$

If we ignore the small volume occupied by solids and liquids, and assume any gases involved in the combustion reaction obey the ideal gas law, then eq 2.5.6 can be rewritten as

$$\Delta H_{\text{comb}} \cong \Delta U_{\text{comb}} + \Delta n_{\text{g}}RT \quad (2.5.7)$$

where Δn_{g} is the change in the number of moles of gas per mole of reaction. For example, for the reaction in eq 2.5.3 $\Delta n_{\text{g}} = 2 - \frac{1}{2} = \frac{3}{2}$. Note that the second term on the right is usually much smaller ($< 1\%$) than the first term.

Phase transitions

A phase transition is the conversion of a substance from one phase to another phase. The most common phase transitions are solid \rightarrow liquid (melting, or fusion), liquid \rightarrow gas (vaporization), and solid \rightarrow gas (sublimation), although for substances with several different solid phases (such as the graphite and diamond forms of carbon) solid \rightarrow solid phase transitions can also occur.

When the two phases involved in a phase transition are in equilibrium then q_p , the amount of heat required for one mole of the phase transition to occur, is equal to the enthalpy change for the phase transition, ΔH_{pt} . When the pressure is equal to 1.000 atm, the phase transition is called the normal phase transition, and the enthalpy change is labeled ΔH_{pt}° . Values for the enthalpy change for a phase transition are, when possible, usually reported at the normal transition point. For example, for water the normal melting point is $T_{fus}^\circ = 0.00\text{ }^\circ\text{C}$, and the normal boiling point is $T_{vap}^\circ = 100.0\text{ }^\circ\text{C}$ (in fact, these two points are used to define the Centigrade scale). Note that not all phase transitions will have a normal transition point. For example, there is never a point where water in both the solid and vapor phase can exist simultaneously and at equilibrium when the pressure is 1.000 atm, and so there is no normal sublimation point for water. Instead, the enthalpy of sublimation is reported at some other point, usually chosen for convenience.

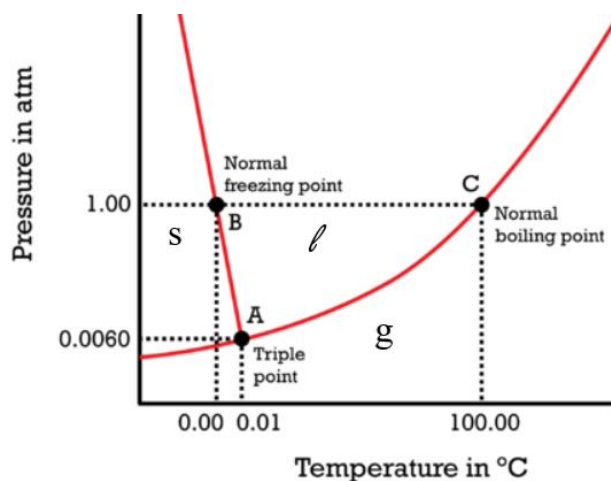


Figure 2. Phase diagram for water. s = solid; ℓ = liquid; g = gas. Point B is the normal melting point and point C is the normal boiling point for water.

Since the process solid \rightarrow gas is equivalent to the processes solid \rightarrow liquid followed by liquid \rightarrow gas, we may say

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}} \quad (2.5.8)$$

Equation 2.5.8 is exact only if all three phase transitions occur at the same temperature and pressure. If we use the values for the normal enthalpy for each phase transition (the value when $p = 1.000$ atm) then eq 2.5.8 is only approximate, since the normal phase transitions will occur at different temperatures (and will not be defined for one or more of the phase transitions).

Estimating ΔH_{rxn} from average bond enthalpies

Consider a chemical reaction where all the reactants and products are in the gas phase (which allows us to assume that molecules do not interact with one another or with solvent molecules)



The process



has the same initial and final state as that in eq 2.5.9, and so has the same value for the change in enthalpy. In terms of the enthalpy change when all of the reactant or product bonds are broken, we may say

$$\Delta H_{\text{rxn}} = [\Sigma (\text{bond enthalpies of reactants})] - [\Sigma (\text{bond enthalpies of products})] \quad (2.5.11)$$

where the contributions of all the bonds being broken are added together. The subtraction of the bond enthalpies of the products is due to the fact that the process of going from atoms to product molecules is bond formation, the reverse of breaking the bonds in the product molecules.

Equation 2.5.11 is exact. However, we usually replace the actual bond enthalpies for the specific bonds in the reactant and product molecules with average bond enthalpies, which represent typical values for a particular type of bond. In that case, eq 2.5.11 becomes

$$\begin{aligned} \Delta H_{\text{rxn}} \cong [\Sigma (\text{average bond enthalpies of reactants})] \\ - [\Sigma (\text{average bond enthalpies of products})] \end{aligned} \quad (2.5.12)$$

Using eq 2.5.12 and a table of average bond enthalpies, the enthalpy change for a gas phase reaction can be estimated (this assumes each reactant and product molecule has a well-defined Lewis structure). For example, for the reaction



we may use the data in Table 1 to estimate the value for ΔH_{rxn} . (Note that it is easiest to count up the number and type of bonds being broken by drawing the Lewis structures for each reactant and product molecule).

Reactant molecules		Product molecules	
10 (C-H)	= 10 (412 kJ/mol)	8 (C-H)	= 8 (412 kJ/mol)
1 (C-C)	= 1 (348 kJ/mol)	2 (C-C)	= 2 (348 kJ/mol)
		1 (H-H)	= 1 (436 kJ/mol)
Total	= 4468 kJ/mol	Total	= 4428 kJ/mol

So the estimated value for the enthalpy of reaction is $\Delta H_{\text{rxn}} \cong 4468 \text{ kJ/mol} - 4428 \text{ kJ/mol} = 20 \text{ kJ/mol}$. This is reasonably close to the value found from the enthalpies of formation of the reactants and products, $\Delta H_{\text{rxn}}^{\circ} = 55.64 \text{ kJ/mol}$.

Table 1 – Average bond enthalpies (all values are in kJ/mol)

H-H	436	C-C	348	C-O	360	N-N	163
C-H	412	C=C	612	C=O	743	N=N	409
N-H	388	C≡C	838	C-F	484	N≡N	945
O-H	463	C-N	305	C-Cl	338	N-O	157
S-H	338	C=N	613	C-Br	276	O-O	146
P-H	322	C≡N	890	C-S	259	O=O	497
F-F	155	Cl-Cl	242	Br-Br	193		

The above method for estimating the value for ΔH_{rxn} is only a fair approximation to the true value for the enthalpy of reaction. However, the method can be modified to improve on the agreement between the estimated and actual value for the reaction enthalpy.