

Chemistry 331

Lectures 13 and 14
Enthalpy

NC State University

Motivation

The enthalpy change ΔH is the change in energy at constant pressure. When a change takes place in a system that is open to the atmosphere, the volume of the system changes, but the pressure remains constant. In any chemical reactions that involve the creation or consumption of molecules in the vapor or gas phase there is a work term associated with the creation or consumption of the gas.

Molar Enthalpy

Enthalpy can be expressed as a molar quantity:

$$H_m = \frac{H}{n}$$

We can also express the relationship between enthalpy and internal energy in terms of molar quantities:

$$H_m = U_m + PV_m$$

For an ideal or perfect gas this becomes:

$$H_m = U_m + RT$$

Usually when we write ΔH for a chemical or physical change we refer to a molar quantity for which the units are kJ/mol.

Enthalpy for reactions involving gases

If equivalents of gas are produced or consumed in a chemical reaction, the result is a change in pressure-volume work. This is reflected in the enthalpy as follows.

$$\Delta H = \Delta U + P\Delta V \quad \text{at const. } T \text{ and } P$$

which can be rewritten for an ideal gas:

$$\Delta H = \Delta U + \Delta nRT \quad \text{at const. } T \text{ and } P$$

The number of moles n is the number of moles created or absorbed during the chemical reaction. For example,



We arrive at this value from the formula

$$\Delta n = n_{\text{products}} - n_{\text{reactants}} = 1 - 2 = -1$$

The temperature dependence of the enthalpy change

Based on the discussion the heat capacity from the last lecture we can write the temperature dependence of the enthalpy change as:

$$\Delta H = C_p \Delta T$$

Note that we can use tabulated values of enthalpy at 298 K and calculate the value of the enthalpy at any temperature of interest. We will see how to use this when we consider the enthalpy change of chemical reactions (the standard enthalpy change). The basic physics of all temperature dependence is contained in the above equation or more frequently in the equation below as molar quantity:

$$\Delta H_m = C_{p,m} \Delta T$$

Another view of the heat capacity

At this point it is worth noting that the expressions for the heat capacity at constant volume and constant pressure can be related to the temperature dependence of U and H , respectively.

$$\Delta H = C_p \Delta T$$

$$\Delta U = C_v \Delta T$$

$$C_p = \frac{\Delta H}{\Delta T} = \left(\frac{\partial H}{\partial T} \right)_p$$

$$C_v = \frac{\Delta U}{\Delta T} = \left(\frac{\partial U}{\partial T} \right)_v$$

The heat capacity is the rate of change of the energy with temperature. The partial derivative is formal way of saying this.

The heat capacity is also a function of temperature

We have treated the heat capacity as a constant up to this point. That is a valid approximation under many circumstances, but only over a limited range of temperature. In the general case the temperature dependence of the enthalpy can be described as:

$$\Delta H = \int_{T_1}^{T_2} C_p(T) dT, \quad C_p(T) = a + bT + \frac{c}{T^2}$$

The parameters a, b, and c are given in Tables. Actually, this expression is readily integrated in the general case to give:

$$\Delta H = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + c\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Enthalpy of physical change

A physical change is when one state of matter changes into another state of matter of the same substance. The difference between physical and chemical changes is not always clear, however, phase transitions are obviously physical changes.

Fusion ΔH_{fus} ΔH_{vap} Vaporization

Solid \Leftrightarrow *Liquid* \Leftrightarrow *Gas*

Freezing ΔH_{freeze} ΔH_{cond} Condensation

Sublimation ΔH_{sub}

Solid \Leftrightarrow *Gas*

Vapor Deposition $\Delta H_{vap\ dep}$

Properties of Enthalpy as a State Function

The fact that enthalpy is a state function is useful for the additivity of enthalpies. Clearly the enthalpy of forward and reverse processes must be related by:

$$\Delta_{forward}H = -\Delta_{reverse}H$$

so that the phase changes are related by:

$$\Delta_{fus}H = -\Delta_{freeze}H$$

$$\Delta_{vap}H = -\Delta_{cond}H$$

$$\Delta_{sub}H = -\Delta_{vap\ dep}H$$

Moreover, it should not matter how the system is transformed from the solid phase to the gas phase. The two processes of fusion (melting) and vaporization have the same net enthalpy as sublimation.

Question

Which is statement is false:

A. $\Delta_{\text{sub}}H > 0$

B. $\Delta_{\text{cond}}H < 0$

C. $\Delta_{\text{fus}}H > 0$

D. $\Delta_{\text{vap}}H < 0$

Additivity of Enthalpies

Because the enthalpy is a state function the same magnitude must be obtained for direct conversion from solid to gas as for the indirect conversion solid to liquid and then liquid to gas.

$$\Delta_{\text{sub}}H = \Delta_{\text{fus}}H + \Delta_{\text{vap}}H$$

Of course, these enthalpies must be measured at the same temperature. Otherwise an appropriate correction would need to be applied as described in the section on the temperature dependence of the enthalpy.

Question

Which statement is true?

A. $\Delta_{\text{sub}}H = \Delta_{\text{fus}}H - \Delta_{\text{vap}}H$

B. $\Delta_{\text{vap}}H = \Delta_{\text{sub}}H - \Delta_{\text{fus}}H$

C. $\Delta_{\text{fus}}H = \Delta_{\text{sub}}H + \Delta_{\text{vap}}H$

D. $\Delta_{\text{vap}}H = \Delta_{\text{sub}}H + \Delta_{\text{fus}}H$

Chemical Change

In a chemical change the identity of substances is altered during the course of a reaction. One example is the hydrogenation of ethene:



The negative value of ΔH signifies that the enthalpy of the system decreases by 137 kJ and, if the reaction takes place at constant pressure, 137 kJ of heat is released into the surroundings, when 1 mol of $\text{CH}_2=\text{CH}_2$ combines with 1 mol of H_2 at 25 °C.

Standard Enthalpy Changes

The reaction enthalpy depends on conditions (e.g. T and P). It is convenient to report and tabulate information under a standard set of conditions.

Corrections can be made using heat capacity for variations in the temperature. Corrections can also be made for variations in the pressure.

When we write ΔH^\ominus in a thermochemical equation, we always mean the change in enthalpy that occurs when the reactants change into the products in their respective standard states.

Standard Reaction Enthalpy

The standard reaction enthalpy, $\Delta_r H^\ominus$, is the difference between the standard molar enthalpies of the reactants and products, with each term weighted by the stoichiometric coefficient.

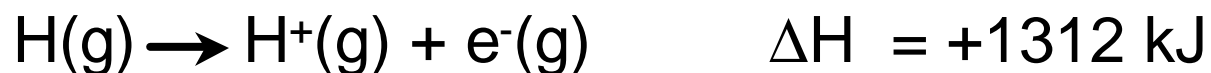
$$\Delta_r H^\ominus = \sum \nu H_m^\ominus(\text{products}) - \sum \nu H_m^\ominus(\text{reactants})$$

The standard state is for reactants and products at 1 bar of pressure. The unit of energy used is kJ/mol.

The temperature is not part of the standard state and it is possible to speak of the standard state of oxygen gas at 100 K, 200 K etc. It is conventional to report values at 298 K and unless otherwise specified all data will be reported at that temperature.

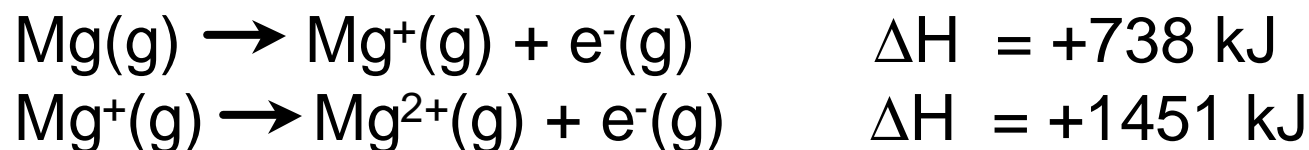
Enthalpies of Ionization

The molar enthalpy of ionization is the enthalpy that accompanies the removal of an electron from a gas phase atom or ion:

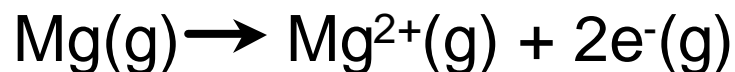


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For ions that are in higher charge states we must consider successive ionizations to reach that charge state. For example, for Mg we have:

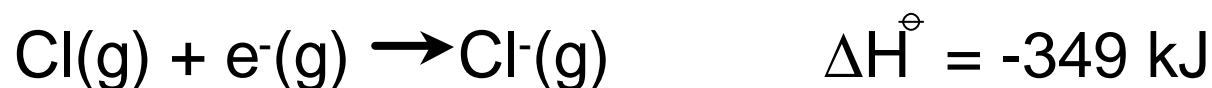


We shall show that these are additive so that the overall enthalpy change is 2189 kJ for the reaction:



Electron Gain Enthalpy

The reverse of ionization is electron gain. The corresponding enthalpy is called the electron gain enthalpy. For example:



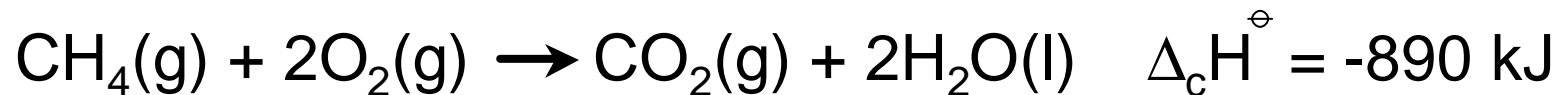
The sign can vary for electron gain. Sometimes, electron gain is endothermic.

The combination of ionization and electron gain enthalpy can be used to determine the enthalpy of formation of salts.

Other types of processes that are related include molecular dissociation reactions.

Enthalpies of Combustion

Standard enthalpies of combustion refer to the complete combination with oxygen to carbon dioxide and water. For example, for methane we have:



Enthalpies of combustion are commonly measured in a bomb calorimeter (a constant volume device). Thus, ΔU_m is measured. To convert from ΔU_m to ΔH_m we need to use the relationship:

$$\Delta H_m = \Delta U_m + \Delta v_{\text{gas}} RT$$

The quantity Δv_{gas} is the change in the stoichiometric coefficients of the gas phase species. We see in the above express that $\Delta v_{\text{gas}} = -2$. Note that H_2O is a liquid.

Question

Fill in the missing stoichiometric coefficients for the combustion reaction:



- A. X=4, Y=8, Z=12
- B. X=8, Y=5, Z=6
- C. X=4, Y=10, Z=6
- D. X=2, Y=1, Z=6

Question

Fill in the missing stoichiometric coefficients for the combustion reaction:



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- B. X=8, Y=5, Z=6**
- C. X=4, Y=10, Z=6
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Question

Determine Δv_{gas} for the reaction as written:



- A. $\Delta v_{\text{gas}} = 3$
- B. $\Delta v_{\text{gas}} = 8$
- C. $\Delta v_{\text{gas}} = -4$
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The quantity Δv_{gas} is the change in the stoichiometric coefficients of the gas phase species. We see in the above express that $\Delta v_{\text{gas}} = -2$. Note that H_2O is a liquid.

Question

What is the work term for expansion against the atmosphere?



- A. $\Delta v_{\text{gas}} RT$
- B. $\Delta U_{\text{m}} + \Delta v_{\text{gas}} RT$
- C. $\Delta U_{\text{m}} - \Delta v_{\text{gas}} RT$
- D. Δv_{gas}

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Hess's Law

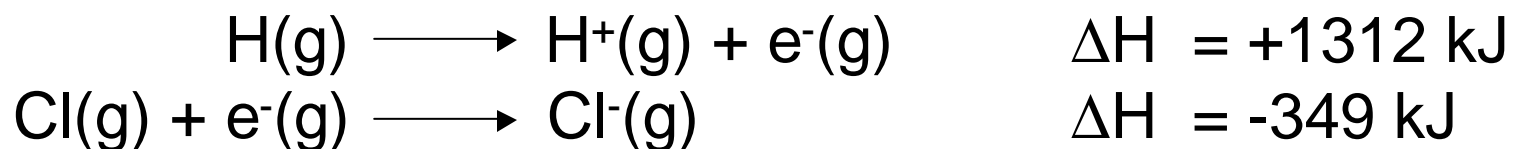
We often need a value of ΔH^\ominus that is not in the thermochemical tables. We can use the fact that ΔH^\ominus is a state function to advantage by using sums and differences of known quantities to obtain the unknown. We have already seen a simple example of this using the sum of ΔH^\ominus of fusion and ΔH^\ominus of vaporization to obtain ΔH^\ominus of sublimation.

Hess's law is a formal statement of this property.

The standard enthalpy of a reaction is the sum of the standard enthalpies of the reactions into which the overall reaction may be divided.

Question

Consider the reactions:

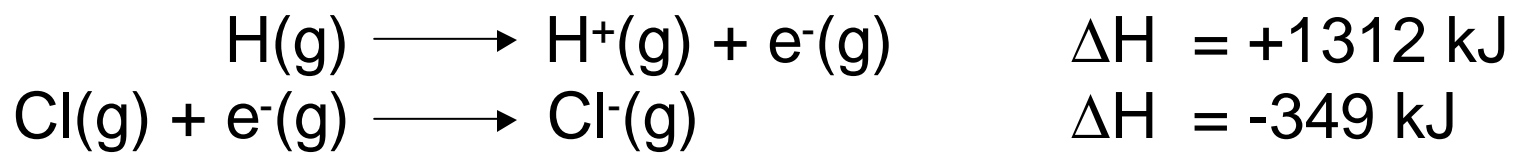


Which statement is true about the charge transfer from H to Cl to form H⁺ and Cl⁻?

- A. $\Delta\text{H} = 963 \text{ kJ}$
- B. $\Delta\text{H} = 1661 \text{ kJ}$
- C. $\Delta\text{H} = 1312 \text{ kJ}$
- D. $\Delta\text{H} = -349 \text{ kJ}$

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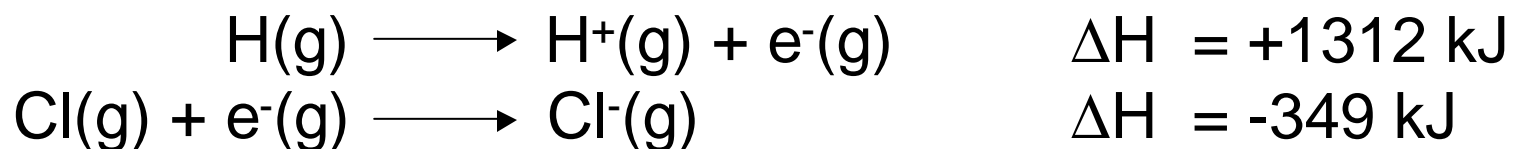


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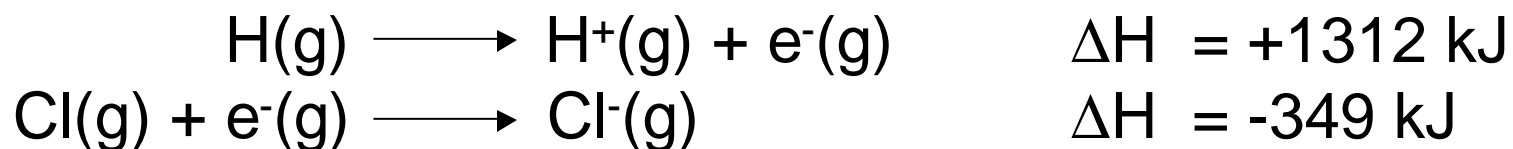


What further information do you need to calculate the enthalpy for the reaction $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{H}^{\text{+}}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$?

- A. ΔH of ionization and ΔH of electron capture
- B. ΔH of formation, ΔH of dissociation and ΔH of solvation
- C. ΔH of ionization and ΔH of solvation
- D. ΔH of dissociation and ΔH of solvation

Question

Consider the reactions:

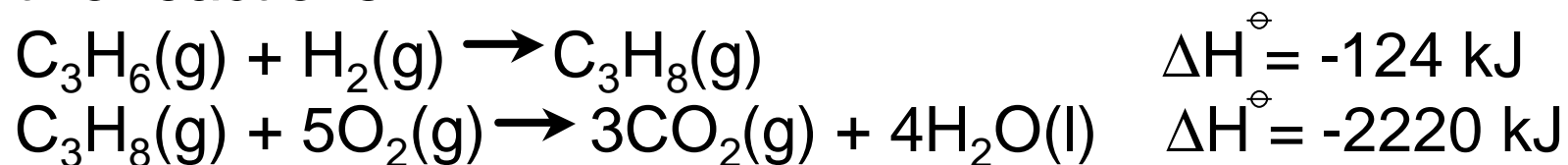


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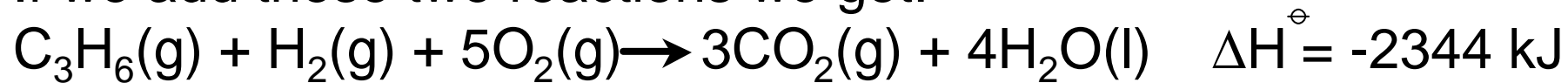
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- B. ΔH of formation, ΔH of dissociation and ΔH of solvation
- C. ΔH of ionization and ΔH of solvation
- D. ΔH of dissociation and ΔH of solvation

Application of Hess's Law

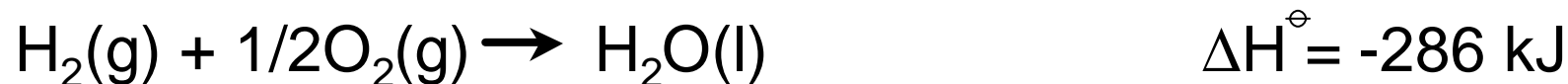
We can use the property known as Hess's law to obtain a standard enthalpy of combustion for propene from the two reactions:



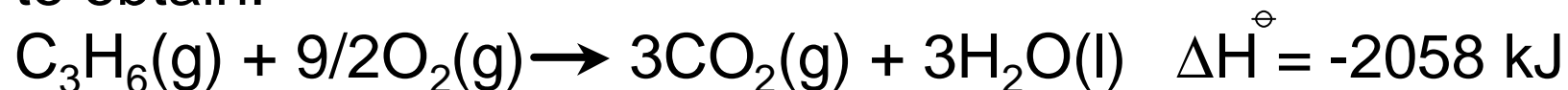
If we add these two reactions we get:



and now we can subtract:



to obtain:



Variation in Reaction Enthalpy with Temperature

Since standard enthalpies are tabulated at 298 K we need to determine the value of the enthalpy at the temperature of the reaction using heat capacity data. Although we have seen this procedure in the general case the calculation for chemical reactions is easier if you start by calculating the heat capacity difference between reactants and products:

$$\Delta_r C_P = \sum \nu C_P(\text{products}) - \sum \nu C_P(\text{reactants})$$

and then substitute this into the expression:

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} \Delta_r C_P dT$$

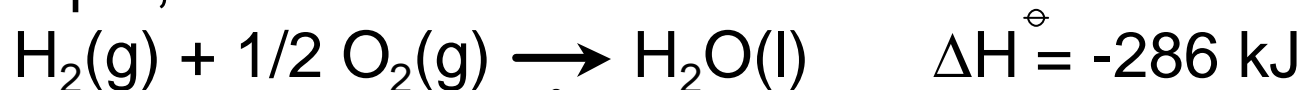
If the heat capacities are all constant of the temperature range then:

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \Delta_r C_P \Delta T$$

Standard Enthalpies of Formation

The standard enthalpy of formation $\Delta_f H^\ominus$ is the enthalpy for formation of a substance from its elements in their standard states. The reference state of an element is its most stable form at the temperature of interest. The enthalpy of formation of the elements is zero.

For example, let's examine the formation of water.



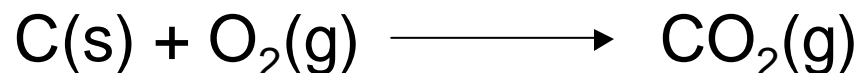
Therefore, we say that $\Delta_f H^\ominus(\text{H}_2\text{O}, \text{l}) = -286 \text{ kJ/mol}$.

Although $\Delta_f H^\ominus$ for elements in their reference states is zero, $\Delta_f H^\ominus$ is not zero for formation of an element in a different phase:



Question

Consider the formation of carbon dioxide at 298 K:

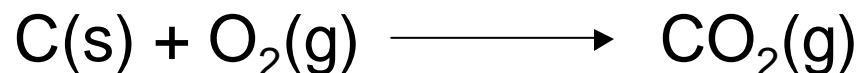


How would you find the heat of formation of oxygen?

- A. Look up $\Delta_f H$ for C(s) and subtract it from that of CO₂.
- B. Look it up the standard thermodynamic tables.
- C. The heat of formation of O₂ is zero by definition.
- D. It is equal to the standard bond energy of two oxygen atoms.

Question

Consider the formation of carbon dioxide at 298 K:

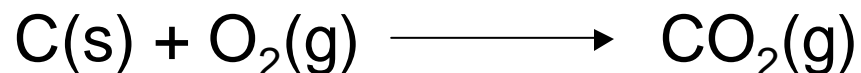


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Question

Consider the formation of carbon dioxide at 150 K:



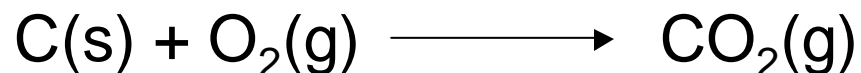
How would you find the heat of formation of CO_2 ?

Apply a correction to the enthalpy from:

- A. Hess's law
- B. the van der Waal's equation of state
- C. ideal gas law
- D. none of the above

Question

Consider the formation of carbon dioxide at 150 K:



How would you find the heat of formation of CO_2 ?

Apply a correction to the enthalpy from:

- A. Hess's law
- B. the van der Waal's equation of state
- C. ideal gas law
- D. none of the above