

# Thermodynamics and Kinetics, CHEM\*2820 Fall 2024

Week 2, Lecture 3

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# Lecture 3 Overview

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**Textbook References:** *Atkins' 12<sup>th</sup> Edition Focus 2C (Thermochemistry)*  
*Atkins' 11<sup>th</sup> Edition Focus 2C (Thermochemistry)*

- Transition enthalpy
- Reaction enthalpy

# Transition Enthalpy

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# Review: Definitions

**Work:** ordered motion against an opposing force, represented by  $w$

$$w = - \int \mathbf{F} \cdot d\mathbf{s} \quad (1)$$

**Heat:** disordered thermal motion, represented by  $q$

**Internal energy:** the total energy that a system possesses. Change in internal energy is equal to the sum of work and heat applied to the system

$$\Delta U = w + q \quad (2)$$

**Enthalpy:** total heat content of a system and is equal to the sum of internal energy and expansion work on the surroundings

$$H = U + pV \quad (3)$$

**Heat capacity:** how the energy of a system changes as a function of temperature

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V, \quad C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad (4)$$

# Review: Enthalpy and Heat

A process that releases energy as heat is **exothermic**, while one that absorbs energy is **endothermic**.

A release of heat into the surroundings at constant pressure signifies a decrease in the enthalpy of a system. Thus, an exothermic process is also **exenthalpic**.

Conversely, because the absorption of heat from the surroundings results in an increase in enthalpy, an endothermic process is also **endenthalpic**.

Exothermic or exenthalpic process:  $\Delta H < 0$

Endothermic or endenthalpic process:  $\Delta H > 0$

# Standard Enthalpy Changes

Changes in enthalpy are normally reported for processes taking place under a set of standard conditions. The **standard enthalpy change**,  $\Delta H^\ominus$ , is the change in enthalpy for a process in which the initial and final substances are in their standard states.

- The **standard state** of a substance at a specified temperature is its pure form at 1 bar (100 000 Pa)

For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 298 K and 1 bar.



# Enthalpies of Physical Change

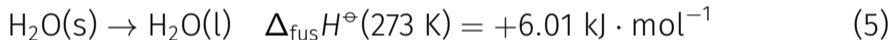
The standard enthalpy change for a reaction or a physical process is the difference in enthalpy between the products and the reactants in their standard states, all at the same specified temperature.

The standard molar enthalpy change that accompanies a change of physical state is called the **standard enthalpy of transition** and is denoted  $\Delta_{\text{trs}}H^\ominus$ . Examples of standard molar enthalpies:

- Standard enthalpy of vaporization,  $\Delta_{\text{vap}}H^\ominus$
- Standard enthalpy of fusion,  $\Delta_{\text{fus}}H^\ominus$

# Standard Enthalpies of Transition

The **standard enthalpy of fusion**,  $\Delta_{\text{fus}}H^\ominus$  is the standard molar enthalpy change accompanying the conversion of a solid into a liquid, as in



Typically these standard enthalpies are given at the transition temperature (the temperature at which the phase transition occurs), however it is sometimes useful to report these values at 298 K.

# Standard Enthalpies

Table 2C.1 Standard enthalpies of fusion and vaporization at the transition temperature\*

	$T_f/K$	Fusion	$T_b/K$	Vaporization
Ar	83.81	1.188	87.29	6.506
C <sub>6</sub> H <sub>6</sub>	278.61	10.59	353.2	30.8
H <sub>2</sub> O	273.15	6.008	373.15	40.656 (44.016 at 298 K)
He	3.5	0.021	4.22	0.084

\* More values are given in the *Resource section*.

Table 2C.2 Enthalpies of reaction and transition

Transition	Process	Symbol*
Transition	Phase $\alpha \rightarrow$ phase $\beta$	$\Delta_{tr}H$
Fusion	$s \rightarrow l$	$\Delta_{fus}H$
Vaporization	$l \rightarrow g$	$\Delta_{vap}H$
Sublimation	$s \rightarrow g$	$\Delta_{sub}H$
Mixing	Pure $\rightarrow$ mixture	$\Delta_{mix}H$
Solution	Solute $\rightarrow$ solution	$\Delta_{sol}H$
Hydration	$X^+(g) \rightarrow X^+(aq)$	$\Delta_{hyd}H$
Atomization	Species( $s, l, g$ ) $\rightarrow$ atoms( $g$ )	$\Delta_{at}H$
Ionization	$X(g) \rightarrow X^+(g) + e^-(g)$	$\Delta_{ion}H$
Electron gain	$X(g) + e^-(g) \rightarrow X^-(g)$	$\Delta_{eg}H$
Reaction	Reactants $\rightarrow$ products	$\Delta_rH$
Combustion	Compound( $s, l, g$ ) + O <sub>2</sub> ( $g$ ) $\rightarrow$ CO <sub>2</sub> ( $g$ ) + H <sub>2</sub> O( $l, g$ )	$\Delta_cH$
Formation	Elements $\rightarrow$ compound	$\Delta_fH$
Activation	Reactants $\rightarrow$ activated complex	$\Delta^\ddagger H$

\* IUPAC recommendations. In common usage, the process subscript is often attached to  $\Delta H$ , as in  $\Delta H_{tr}$  and  $\Delta H_f$ . All are molar quantities.

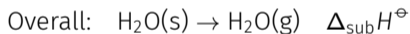
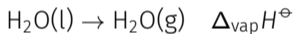
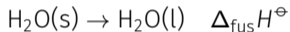
## Path Independence of $\Delta H^\ominus$

Recall that enthalpy is a **state function**, which means that a change in enthalpy is independent of the path between the two states.

**Important:** this means that we can compute the enthalpy of any change in state! That is, as long as we can construct a path from the initial to the final state, and the enthalpies of all steps are known.

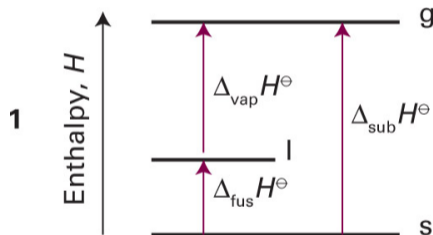
# Path Independence of $\Delta H^\ominus$

Suppose we would like to find the standard enthalpy of sublimation ( $\Delta_{\text{sub}}H^\ominus$ ) for water, but only know the standard enthalpies of fusion ( $\Delta_{\text{fus}}H^\ominus$ ) and vaporization ( $\Delta_{\text{vap}}H^\ominus$ ). We note that

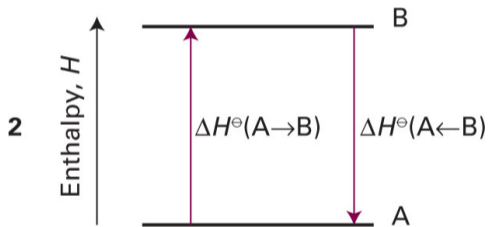


Because the initial and final states are the same in both cases regardless of whether the system goes through a single step or two steps, we know that

$$\Delta_{\text{sub}}H^\ominus = \Delta_{\text{fus}}H^\ominus + \Delta_{\text{vap}}H^\ominus \quad (6)$$



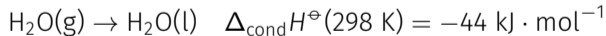
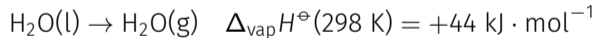
# Path Independence of $\Delta H^\ominus$



It follows that the standard enthalpy change of a process in reverse is the negative of the standard enthalpy change of the forward process

$$\Delta H^\ominus(A \rightarrow B) = -\Delta H^\ominus(B \rightarrow A) \quad (7)$$

For example



# Reaction Enthalpy

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# Standard Reaction Enthalpies

The standard reaction enthalpy method is specified per mole of each species multiplied by the coefficient in the equation



For a reaction of the form



the standard reaction enthalpy would be

$$\Delta_r H^\ominus = [3H_m^\ominus(\text{C}) + H_m^\ominus(\text{D})] - [2H_m^\ominus(\text{A}) + H_m^\ominus(\text{B})] \quad (10)$$

where  $H_m^\ominus(\text{X})$  corresponds to the standard molar enthalpy of species X at the temperature of interest.



# Standard Reaction Enthalpies

Definition of **standard reaction enthalpy**

$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu H_m^\ominus - \sum_{\text{Reactants}} \nu H_m^\ominus \quad (11)$$

where in each case the molar enthalpies of the species are multiplied by their stoichiometric coefficients  $\nu$ . Note that in practice, we do not work with absolute enthalpies but relative enthalpies.

# Hess's Law

The standard reaction enthalpy is the sum of the values for the individual reactions into which the overall reaction may be divided.

Note that we don't necessarily need each step to be achievable in practice as long as the overall chemical equations balance.

The utility of Hess's Law is similar to our example for water sublimation earlier: to obtain the enthalpy of an unknown reaction, we can add up the enthalpies of a few known reactions that yield the net reaction in question.

# Hess's Law

For example, suppose we would like to calculate the enthalpy of combustion for propene ( $C_3H_6$ ), and we know the enthalpies of propene hydrogenation, propane combustion, and water formation.

We would write out the chemical equation for each step so that they add up to the overall reaction for propene combustion, then take the sum of all enthalpies to obtain the net result.

Reaction	$\Delta_r H^\ominus$ (kJ · mol <sup>-1</sup> )
$C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g)$	-124
$C_3H_8(g) + 5 O_2(g) \rightarrow 3 CO_2(g) + 4 H_2O(l)$	-2220
$H_2O(l) \rightarrow H_2(g) + \frac{1}{2} O_2(g)$	+286
$C_3H_6(g) + \frac{9}{2} O_2(g) \rightarrow 3 CO_2(g) + 3 H_2O(l)$	-2058

# Defining Standard Enthalpies and States

The **standard enthalpy of formation**,  $\Delta_f H^\ominus$ , of a substance is the standard reaction enthalpy for the formation of the compound from its elements in their reference states.

The **reference state** of an element is its most stable state at the specified temperature and 1 bar (100 kPa or 0.9869 atm). At 298 K, the reference state of

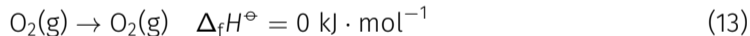
- Nitrogen is gaseous  $N_2$
- Mercury is metallic liquid Hg
- Carbon is solid graphite

# Standard Enthalpies of Formation

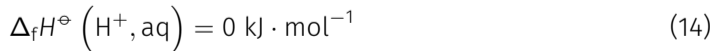
Standard enthalpies of formation are expressed as enthalpies per mole of molecules or formula units (for periodic systems) of the compound. Take liquid benzene as an example



By definition, the standard enthalpies of formation of elemental compounds in their reference states are zero at all temperatures



For solvated ions, we define the formation enthalpy of solvated protons to be zero at all temperatures



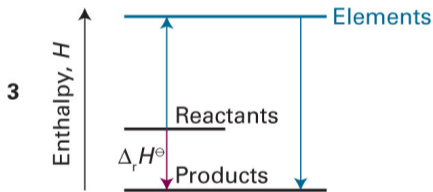
# Standard Enthalpies of Reaction

Now we can frame the standard reaction enthalpy definition in terms of the standard formation enthalpy.

We can reference each species in a chemical reaction to their standard formation enthalpy, and subtract these standard formation enthalpies appropriately to get the reaction enthalpy.

Equation 11 can thus be modified to

$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu H_f^\ominus - \sum_{\text{Reactants}} \nu H_f^\ominus \quad (15)$$



# Conclusion

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We have

- defined enthalpies of transition, which encompasses many processes
- examined enthalpies of formation and reaction in detail
- established a standard method for obtaining reaction enthalpies



# Thank You!

**Next Topic:** Internal Energy and Expansion Work

We will resume the Class Notebook format next time.