

A First Course on Kinetics and Reaction Engineering

Unit 2. Reaction Thermochemistry

Overview

This course is divided into four parts, I through IV. Part I reviews some topics related to chemical reactions that most students will have encountered in previous chemical engineering courses. Unit 2 considers the heat that is absorbed or released when a chemical reaction occurs. This is a subject that typically is first studied in an introductory thermodynamics course or a course in physical chemistry. Here it is assumed that the reader has taken such a course, so only a brief review is presented. The primary focus is how to write an expression for the heat of a reaction. In addition, the unit also considers the temperature rise associated with an exothermic reaction that occurs adiabatically and the calculation of the Gibbs free energy for a reaction at 298 K. For a more thorough discussion of these topics a textbook devoted to thermodynamics should be consulted (1-4). The concepts that are reviewed here will be utilized repeatedly throughout the remainder of the course, and therefore it is critically important to master them before proceeding to Parts II, III and IV.

Learning Objectives

Upon completion of this unit, you should be able to define, in words, the following terms:

- standard heat of reaction, endothermic reaction, exothermic reaction, state function, adiabatic process, adiabatic temperature change/rise, sensible heat, latent heat

Upon completion of this unit, you should be able to write the defining equation for the following quantities:

- standard heat of reaction at 298 K from heats of formation or from heats of combustion, standard Gibbs free energy of reaction at 298 K from free energies of formation, and standard heats of reaction at any temperature T from the standard heat of reaction at 298 K and necessary heat capacities and latent heats

Upon completion of this unit, you should be able to perform the following specific tasks and be able to recognize when they are needed and apply them correctly in the course of a more complex analysis:

- Explain the meaning of the heat of reaction for a reaction that does not proceed all the way to 100% conversion
- Find data for heats of formation, free energies of formation, heats of combustion and heat capacities using standard reference sources
- Calculate heats of reaction at any temperature and free energy changes at 298 K (see Examples 2.1, 2.2 and 2.4)
- Calculate the adiabatic temperature change given the reactions that occur, starting composition and appropriate measures of the reactions' progress (see example 2.3)

Information

Heats of Reactions. Consider a steady-state flow system involving a single reaction where a stoichiometric amount of each reactant is being fed. The reactants are being fed at constant temperature

and pressure. Inside the system complete reaction takes place so that a stoichiometric amount of each product emerges from the system. These products leave the system at the same temperature and pressure as the reactants entered. The system is stationary, has no moving boundaries or other means of receiving or supplying work, and the kinetic and potential energy of the reactants are the same as those of the products. The heat that must be added to this system for the process to occur as just described is called the heat of reaction. The symbol ΔH_j is used to represent the heat of reaction j . If ΔH_j is a positive number (heat must be added to the system), reaction j is said to be *endothermic*. If ΔH_j is a negative number (heat must be removed from the system), reaction j is said to be *exothermic*.

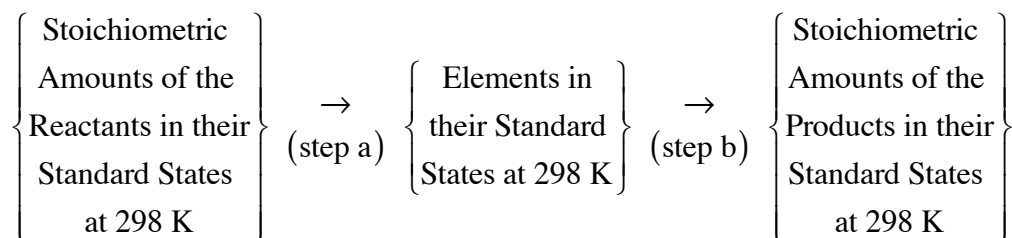
The units of a heat of reaction are typically kJ mol^{-1} , or something equivalent. The mole unit in the heat of reaction sometimes leads to confusion. The mole in the units of heat of reaction is actually a mole of reaction extent (ξ_j , Unit 1) for the reaction as written. In this way, the value of the heat of reaction is tied to the set of stoichiometric coefficients that are used to balance the chemical reaction. This must be true, so that the energy per mole of any one particular species is the same, regardless of how the reaction is written. (After all, the reacting molecules have no idea how the reaction equation has been written!) One other aspect of the heat of reaction also causes confusion at times. Quite often, in a real reactor, the reaction does not or cannot go all the way to completion. This is accounted for when the energy balance for the reactor is written, **not** by adjusting the value of the heat of reaction. The heat of reaction is still defined as the heat that must be added for **complete** stoichiometric reaction, as written.

Enthalpy, and consequently the heat of reaction, is a *state function*. This means that the heat of reaction depends only upon the initial and final conditions of the process and not upon the path that was followed in moving from the initial condition to the final condition. Because enthalpy is a state function, it is not necessary to measure the heat of reaction at every possible set of conditions. The heat of reaction at some arbitrary set of conditions can be calculated from the heat of reaction at a standard set of conditions and from thermodynamic properties of the reactants and products.

Before performing such calculations a standard state is specified for each species involved in the reaction. There are many different standard states that have been proposed and used. For a liquid or a solid, one common standard state is the pure material as it exists at 1 atm and the temperature of interest. For a gas, the standard state is commonly the ideal gas state at 1 atm pressure and the temperature of interest. A superscript 0 denotes an enthalpy change involving materials in their standard states.

It is not even necessary to tabulate data for every known reaction, j . It is only necessary to tabulate heats of reaction for certain special reactions. One such set of special reactions is called formation reactions. The *standard heat of formation at 298 K* of some species i , $\Delta H_{f,i}^0(298 \text{ K})$, is the heat of the reaction in which one mole of species i (in its standard state) is synthesized from the elements that comprise it (in their standard states) at 298 K. Standard heats of formation at 298 K are tabulated for many chemicals in various handbooks; selected lists often appear in thermodynamics textbooks, too. Tables of this type should indicate the standard state that has been used for each of the elements.

Most reactions of interest are not formation reactions. Because enthalpy is a state function, the *standard heat of a reaction at 298 K* can be calculated using any pathway that begins with stoichiometric amounts of the reactants in their standard states at 298 K and ends with stoichiometric amounts of the products in their standard states at 298 K. The pathway may even be hypothetical. Scheme 2.1 details one such pathway that involves two steps, a and b. The pathway shown in Scheme 2.1 allows the standard heat of a reaction to be calculated from the standard heats of formation of the reagents.



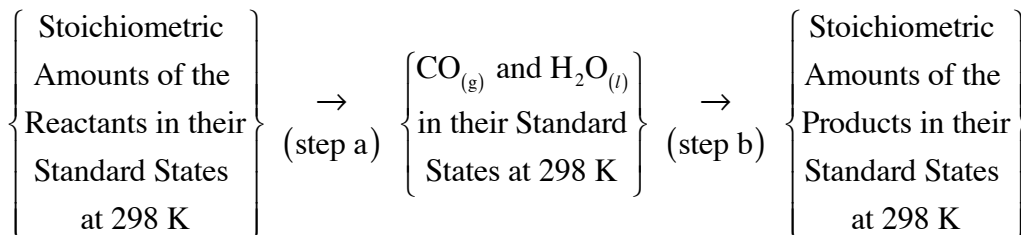
Scheme 2.1. Pathway for a reaction occurring at 298 K that can be useful when calculating the standard heat of that reaction.

In step a of Scheme 2.1 each reactant decomposes to yield the elements that comprise it. This is the reverse of the formation reaction for each reactant. Thus, the heat of reaction per mole of each reactant, i , in step a is equal to $-\Delta H_{f,i}^0(298 \text{ K})$. The total heat of reaction for step a is the product of the number of moles of reactant i and $-\Delta H_{f,i}^0(298 \text{ K})$, summed over all reactants i . Scheme 2.1 calls for a stoichiometric amount of each reactant. Therefore, the number of moles of each species is equal in magnitude to its stoichiometric coefficient. Step b of Scheme 2.1 is the formation of a stoichiometric amount of each product from the elements that comprise it. Thus, for any one product, i , in step b, the heat of reaction per mole is equal to $\Delta H_{f,i}^0(298 \text{ K})$. The total heat of reaction for step b is the product of the number of moles of each product i and $\Delta H_{f,i}^0(298 \text{ K})$, summed over all products i . Adding the heats of reaction for step a and step b (and obeying the sign convention for stoichiometric coefficients) gives the standard heat of reaction j at 298 K, equation (2.1).

$$\Delta H_j^0(298 \text{ K}) = \sum_{\substack{i=\text{all} \\ \text{species}}} v_{i,j} \Delta H_{f,i}^0(298 \text{ K}) \quad (2.1)$$

An alternative to using standard heats of formation to calculate standard heats of reaction is using standard heats of combustion. The *standard heat of combustion at 298 K* of some species i , $\Delta H_{c,i}^0(298 \text{ K})$, is the heat of the reaction in which species i is completely oxidized by O_2 at 298 K, usually producing CO_2 and $\text{H}_2\text{O}_{(l)}$ (with all species in their standard states). Standard heats of combustion are tabulated in handbooks and textbooks, just as standard heats of formation are. Standard heats of combustion are particularly convenient for use with hydrocarbons. If species i contains elements other than C, O and H, it becomes necessary to specify additional combustion products and their standard states.

Again, any pathway that begins with stoichiometric amounts of the reactants in their standard states and ends with stoichiometric amounts of the products in their standard states can be used to find the standard heat of reaction. Scheme 2.2 gives a pathway that is useful when using standard heats of combustion.



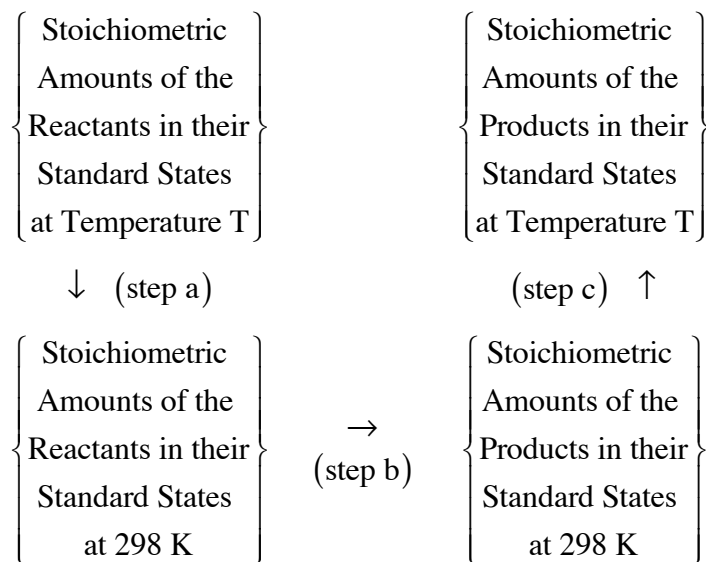
Scheme 2.2. Another pathway for a reaction occurring at 298 K that can be useful when calculating the standard heat of that reaction.

Step a of the pathway in Scheme 2.2 is the combustion of each reactant. Thus the heat of this step is equal to the product of a stoichiometric number of moles of reactant i and the standard heat of combustion of species i , summed over all reactants. Similarly, step b is the reverse of the combustion reaction for each of the products. The heat of step b is equal to the product of a stoichiometric number of moles of species i and the negative of the standard heat of combustion, summed over all products. Combining the heats for step a and step b, and using stoichiometric amounts of all species, gives an expression for the standard heat of reaction j at 298 K, equation (2.2). Notice there is a minus sign in equation (2.2) but not in equation (2.1).

$$\Delta H_j^0(298 \text{ K}) = \sum_{\substack{i=\text{all} \\ \text{species}}} v_{i,j} (-\Delta H_{c,i}^0(298 \text{ K})) \quad (2.2)$$

The standard heat of reaction at a temperature, T , other than 298 K can be calculated using the pathway shown in Scheme 2.3. This is again possible because enthalpy is a state function. It entails cooling the reactants from the temperature, T , to 298K, reaction to form the products at 298 K, and heating the products from 298 K to the temperature, T . Notice that the enthalpy change in step b of the pathway shown in Scheme 2.3 is equal to $\Delta H_j^0(298 \text{ K})$, and the calculation of this quantity was just described.

Step a of Scheme 2.3 simply involves heating or cooling the stoichiometric amounts of reactants from temperature T to 298 K. Similarly, step c involves cooling or heating the products from 298 K back to the original temperature of the reactants. Since the species remain in their standard state during these heating and cooling steps they are always at 1 atm. Thus there is no need to account for pressure effects. The heat capacity at constant pressure is used to find the change in enthalpy during heating and cooling.



Scheme 2.3. Pathway for a reaction occurring at a temperature, T , other than 298 K, that can be used to calculate the standard heat of that reaction at temperature T , provided none of the reactants or products undergo a phase change in the temperature interval from 298 K to T .

Since the definition of heat of reaction calls for a stoichiometric mixture of reactants and of products, the number of moles of each species involved in the pathway shown in Scheme 2.3 is equal in magnitude to its stoichiometric coefficient. The stoichiometric coefficient of a reactant is negative, and the stoichiometric coefficient of a product is positive. With this sign convention the heat of step a can be calculated using equation (2.3) provided **no phase changes occur between T and 298 K**. If the heating or cooling in this step passes through the normal boiling point, melting point or other phase transition point of a species, then the latent heat for the phase change must also be included. Equation (2.3) assumes no such phase changes occur.

$$\Delta H_{T \rightarrow 298 \text{ K}}^0 = \sum_{\substack{i = \text{all} \\ \text{reactants}}} \left(-v_{i,j} \int_T^{298 \text{ K}} \hat{C}_{p,i} dT \right) = \sum_{\substack{i = \text{all} \\ \text{reactants}}} \left(v_{i,j} \int_{298 \text{ K}}^T \hat{C}_{p,i} dT \right) \quad (2.3)^1$$

In equation (2.3), $\hat{C}_{p,i}$ represents the molar heat capacity of species i at constant pressure. The summation is taken only over the reactants. In general $\hat{C}_{p,i}$ is a function of temperature. The heat of step c is found similarly using equation (2.4), again provided **no phase changes occur between T and 298 K**. In equation (2.4) the summation is taken only over the products.

$$\Delta H_{298 \text{ K} \rightarrow T}^0 = \sum_{\substack{i = \text{all} \\ \text{products}}} \left(v_{i,j} \int_{298 \text{ K}}^T \hat{C}_{p,i} dT \right) \quad (2.4)^2$$

¹ This equation is only valid if there is no phase change between 298 K and T .

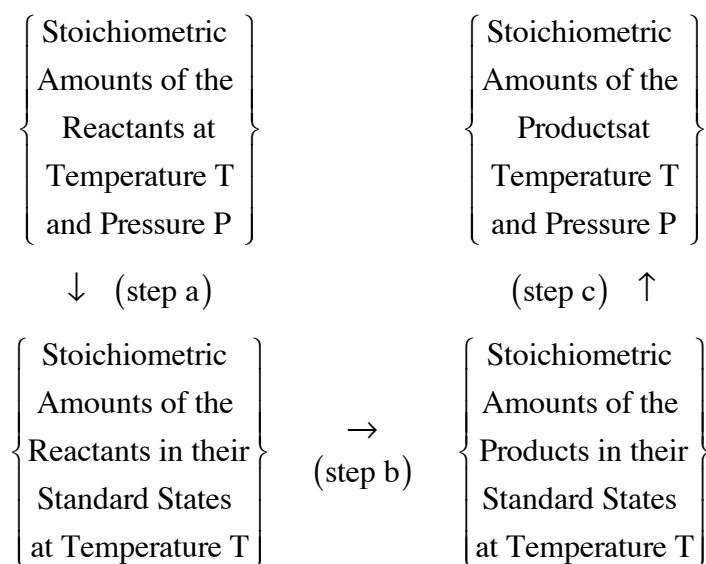
² This equation is only valid if there is no phase change between 298 K and T .

The standard heat of reaction at temperature T is then found by adding the heats of step a, step b, and step c of the pathway shown in Scheme 2.3. The result is an expression, equation (2.5), for calculating the standard heat of reaction at any temperature (provided **no phase changes occur between T and 298 K**). In equation (2.5), equations (2.3) and (2.4) were combined so that the summation in equation (2.5) is taken over all species. It is important to remember that the stoichiometric coefficients of reactants are negative when using equation (2.5).

$$\Delta H_j^0(T) = \Delta H_j^0(298 \text{ K}) + \sum_{\substack{i=\text{all} \\ \text{species}}} \left(v_{i,j} \int_{298 \text{ K}}^T \hat{C}_{p,i} dT \right) \quad (2.5)^3$$

As already noted, if one or more of the species involved in the reaction undergoes a phase change in the temperature interval between 298 K and T , it is then necessary to add the latent heat associated with the phase change. It is also important to note that the heat capacity usually changes when a phase change takes place. That is, for example, the heat capacity of ice differs from that of liquid water which differs from that of steam. As a consequence, the heating or cooling step may need to be broken into two terms, one using the heat capacity that is appropriate up to the temperature of the phase change and the other using the heat capacity appropriate to the phase present beyond the phase change temperature.

The procedure for the calculation of the actual (not standard) heat of reaction makes use of the pathway shown in Scheme 2.4.



Scheme 2.4. A pathway that can be used to calculate the actual heat of a reaction if the standard heat of that reaction is known.

Step b in Scheme 2.4 is just the standard heat of reaction at temperature T . The heat of step b is found using the procedure already described. Step a and step c involve the transformation from the actual

³ This equation is only valid if there is no phase change between 298 K and T .

state to the standard state. The heat for these steps can include various contributions. For example, a term might be needed to account for the heat involved in mixing the pure components (the standard state) to generate a stoichiometric mixture. If the actual reaction involved gases at elevated pressure, a term would be needed for the heat involved in going from the elevated pressure to 1 atm (ideal gas). Latent heat terms would also be needed to account for any phase changes in going from the actual state to the standard state.

Adiabatic Temperature Rise. An *adiabatic process* is one that takes place without any heat input or removal. It was noted in Unit 1 that chemical reactions entail the making and breaking of chemical bonds. The formation of chemical bonds is accompanied by the release of energy, usually in the form of heat, and similarly the breaking of chemical bonds requires the input of energy, and again the energy is usually supplied in the form of heat. The net energy required for breaking and forming all the bonds involved in a given reaction is almost never equal to zero. The net difference between the required energy input and energy release is directly related to the standard heat of reaction.

Consider an exothermic chemical reaction that takes place adiabatically in a system with no shafts or moving boundaries. By definition, no heat enters or leaves the system because we are considering an adiabatic process. In addition, since there are no shafts or moving boundaries, no energy enters or leaves the system in the form of work. Nonetheless, as the reaction takes place, the standard heat of reaction is released (since we are considering an exothermic reaction). That heat cannot leave the system (since it is adiabatic), but it has to go somewhere. (Think of heat as energy that is in motion from one place to another. It can't just stop and stay where it is; at least not in the form of heat.) The only place the heat of reaction can "go" is into the molecules making up the system. Thus, the heat released by the exothermic reaction is converted into internal molecular energy. From a macroscopic perspective the result is that the temperature of the system increases. That is, the heat released by the reaction is used to raise the temperature of the reacting system.

Heat that is converted into internal molecular energy in a system and causes the temperature of that system to rise is often referred to as *sensible heat*. Heat can also be converted into internal molecular energy without causing a change in temperature if, instead, it causes a change of phase. Heat that is converted into internal molecular energy in a system, resulting in a phase change at constant temperature is often referred to as *latent heat*. Return now to our consideration of an exothermic chemical reaction that takes place adiabatically in a system with no shafts or moving boundaries. As the heat of reaction is released, it can't leave the system, and so it is converted into sensible heat, causing the temperature of the system to rise. If, as the temperature rises, the system, or a component of the system, reaches its normal boiling, melting, or other phase transition temperature, the heat being released starts being converted into latent heat. If the entire system, or all of the component, changes phases without using up all of the heat released by the reaction, then the remaining heat of reaction will again become sensible heat, but now associated with the new phase of the system.

When the reaction process ends, the system will be at a new temperature. In the case of an exothermic reaction, this temperature will be greater than the starting temperature, and the change in temperature is referred to as the adiabatic temperature rise. Instead of considering an exothermic

reaction, we could have considered an endothermic reaction. In that case, sensible and/or latent heat of the system would need to be taken from the system in order to supply the necessary heat of reaction. For an endothermic reaction the system temperature will therefore decrease, resulting in an adiabatic temperature drop. For the remainder of this discussion, we can generalize by simply referring to the adiabatic temperature change, noting that if the reaction is exothermic it will be a rise and if the reaction is endothermic it will be a drop.

Notice that one doesn't need to know anything about the container holding the system (in our case, the reactor) other than it operates adiabatically and without any shafts or moving boundaries. We can analyze the adiabatic temperature change using only thermodynamic quantities. Our usual goal is to calculate the adiabatic temperature change given (i) a starting composition and temperature (ii) the reactions taking place and (iii) the extents of a complete mathematically independent sub-set of those reactions (or equivalently, the final composition - the final temperature is unknown). The key to the analysis is that the process is adiabatic so that the net heat released (or consumed) by the reactions taking place must just equal the sensible and latent heat added to (removed from) the system.

The essential point is that the heat released or absorbed by reaction must just equal the sensible and latent heats. Furthermore, since enthalpy is a state function, we do not need to follow the exact same pathway as the system does; we simply need to start at the same initial conditions and end at the same final conditions. For analysis purposes, it is convenient to use a pathway where the reactions first occur isothermally at the initial temperature and then the resulting product mix is heated (or cooled) to the final temperature. The net ΔH for the two steps is then set equal to zero, giving an implicit equation for the final temperature, equation (2.6). Notice that the summation on the left-hand side of equation (2.6) is not taken over all of the reactions taking place; the summation only includes a complete mathematically independent sub-set of the reactions taking place. Notice also that the summation on the right hand side of equation (2.6) is taken over all species present in the system, not just the reactants and products, and it assumes that no phase changes occur between T_1 and T_2 .

$$\sum_{j=1}^{N_{ind}} \xi_j (-\Delta H_j(T_1)) = \sum_{\substack{i=all \\ species}} \int_{T_1}^{T_2} \hat{C}_{p,i} (n_i^0 + \nu_{i,j} \xi_j) dT \quad (2.6)^4$$

In equation (2.6) the heats of reaction are evaluated at the initial temperature, T_1 , the heat capacities, $\hat{C}_{p,i}$, are generally functions of temperature and the other quantities (initial moles, stoichiometric coefficient and extent of reaction) are defined as in Unit 1. Two types of analysis are common in reaction engineering. In the first, all items appearing in equation (2.6), except for T_2 , are known or can be found in reference handbooks, and the equation can be used to calculate the value of the final temperature, T_2 . In the other common situation, neither the final temperature nor the extents of reaction are known. In this case, equation (2.6) provides a relationship between the final temperature and

⁴ This equation is only valid for an adiabatic reaction where no phase change occurs between T_1 and T_2 .

the extents of reaction. As discussed in Unit 1, other reaction progress variables can be calculated from the extents of reaction.

Free Energies of Reactions at 298K. Chemical reaction equilibrium is the topic of Unit 3. In that unit, the calculation of equilibrium constants will be reviewed. Equilibrium constants for reactions are calculated using the change in the standard Gibbs free energy, or simply the standard free energy change, $\Delta G_j^0(298\text{ K})$. The Gibbs free energy is like enthalpy in that it is a state function. Again, a change in the value of a state function depends only upon the initial and final conditions of the process and not upon the path that was followed in moving from the initial condition to the final condition.

Since equilibrium constants are very commonly used in thermodynamics and since the calculation of an equilibrium constant makes use of the standard free energy change for the reaction, you will usually find standard free energies of formation tabulated in the same way that standard enthalpies are tabulated. You will typically find them in the same reference sources, too. This means that some of the equations developed earlier in this unit can be used to calculate the standard free energy change for a reaction. In particular, after substituting the Gibbs free energy in place of the enthalpy in equation (2.1), the resulting equation (2.7) can be used to compute the standard free energy change at 298 K for a reaction from the standard free energies of formation of the reagents.

$$\Delta G_j^0(298\text{ K}) = \sum_{\substack{i=\text{all} \\ \text{species}}} \nu_{i,j} \Delta G_{f,i}^0(298\text{ K}) \quad (2.7)$$

The variation of the Gibbs free energy with temperature is not the same as the variation of the enthalpy with temperature. As a consequence it is **not** possible to replace H with G in equations (2.3), (2.4) or (2.5) and then use them to calculate the free energy change at temperatures other than 298 K. It turns out that for our purposes in this first kinetics and reaction engineering course, we will not need the value of the standard Gibbs free energy change at any temperature other than 298 K. This unit has reviewed how to calculate the standard free energy change at 298 K and the standard heat of reaction as a function of T . Unit 3 will review how these quantities are used in the calculation of equilibrium constants.

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