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CHEMICAL EQUILIBRIUM
USING "REACTION TEMPERATURE" AND SPREADSHEET

by

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Abstract

One of the formidable tasks in teaching thermodynamics to students in Mechanical Engineering is to explain what chemical equilibrium is. We have found that, by introducing a "reaction temperature," or "reaction potential," and by using the analogy between chemical equilibrium and thermal equilibrium, the students learn readily the direction of a chemical reaction toward an equilibrium state, in a similar manner as heat transfer in a medium in the direction of decreasing temperature, until the medium attains an equilibrium temperature if it is left alone. This paper presents the concept of reaction temperature/potential with illustrative examples using a spreadsheet that help students understand chemical equilibrium.

Nomenclature

\( G \)    Gibbs function, eq. (8), kJ
\( \bar{g}_i \) partial molal Gibbs function of component \( i \), eq. (12), kJ/kmol
\( H \) enthalpy, kJ
\( \bar{h}_i \) specific enthalpy of component \( i \), kJ/kmol
\( K \) equilibrium constant, eq. (30)
\( n \) total number of moles of mixture, kmol
\( n_i \) number of moles of component \( i \), kmol
\( p \) pressure, atm
\( p_i \) partial pressure of component \( i \), atm
\( p_{ref} \) reference pressure, 1 atm
\( Q \) heat transfer, kJ
\( \bar{R} \) universal gas constant, 8.314 kJ/(kmol.K)
\( S \) entropy, kJ/K
\( \bar{s}_i \) specific entropy of component \( i \), kJ/(kmol.K)
\( T \) temperature, K
\( T_c \) temperature of cold water stream, K
Introduction

The objective of this paper is to introduce the analogy between thermal equilibrium and chemical equilibrium to help engineering students at the undergraduate level understand the abstract concept of chemical equilibrium. We will define a "reaction temperature" or "reaction potential" such that, during a chemical reaction, the reaction temperature/potential of the reactants decreases and that of the products increases. An equilibrium state is reached when the reaction temperature/potential of the reactants and that of the products are the same. Thus, reaction temperature/potential difference "drives" a chemical reaction in a certain direction, in a similar manner as a thermal potential or temperature difference drives heat transfer in the direction of decreasing temperature.

We have introduced thermal/chemical equilibrium analogy in our undergraduate thermodynamics classes at Texas A&M University and have noticed significant improvement of our students' understanding of the concept of chemical equilibrium. Our students have used reaction temperature/potential along with the Quattro-Pro spreadsheet to determine, without using equilibrium constants, the directions of chemical reactions and the compositions of mixtures at chemical equilibrium. Our students generally felt that the thermal/chemical equilibrium analogy made sense, the reaction temperature/potential concept was easy to follow, and that the calculation procedure was quite straightforward.

This paper is not intended to be a research paper. We prepare the manuscript for undergraduate engineering students who have had some thermodynamics background, and for instructors who may consider introducing the thermal/chemical equilibrium analogy and reaction temperature/potential concepts to students in their thermodynamics classes. Such concepts are not covered in any of the widely-adapted undergraduate thermodynamics texts, such as [1 - 6].

Thermal Reactor

Let us consider the transfer of heat from a hot water stream to a cold water stream in a long parallel flow heat exchanger. If the outer walls are well insulated and
the temperatures of the two water streams may be monitored along the heat exchanger, the temperature distributions would be as shown qualitatively in Fig. 1. The temperature of the hot water stream, \( T_h \), drops and that of the cold water stream, \( T_c \), rises along the heat exchanger, as heat is transferred from the hot water stream to the cold water stream. Eventually, when \( T_h = T_c \), we say that a thermal equilibrium is reached between the hot and cold water streams.

According to the Second Law of Thermodynamics, a system that is initially in a state of non-equilibrium reaches equilibrium eventually if it is left alone. The hot and cold water streams are initially in a state of non-equilibrium at the inlets. They attain a thermal equilibrium in the heat exchanger when \( T_h = T_c \). Further downstream, the temperatures of the two water streams remain constant and there is no heat transfer between the two streams. If there are minute variations of \( T_h \) and \( T_c \) locally after the hot and cold water streams have attained a thermal equilibrium, a small amount of heat may flow from one stream to the other, and we may say that heat is transferred reversibly between the two streams.

After the two water streams attain a thermal equilibrium in the heat exchanger, it is not possible for \( T_h \) to continue to drop and/or for \( T_c \) to continue to rise along the heat exchanger. Such a scenario violates the Second Law.

**Chemical Reactor**

Now consider the chemical reactor given in Fig. 2. Five kilomoles of carbon monoxide, \( CO \), 3 kmol of oxygen, \( O_2 \), and 2 kmol of carbon dioxide, \( CO_2 \), at 3,000 K and 1 atm enter the reactor separately. Let us assume that the reactor is very long and that the velocities of the gases are low such that there is more than enough time for the gases to react in the reactor before the products exit the reactor. Let us also assume that the pressure drop along the reactor is negligible and that the temperature of the mixture is maintained constant along the reactor by removing or adding heat. If we could monitor the amounts of \( CO \), \( O_2 \) and \( CO_2 \) along the reactor, the respective amounts at several stations would be as shown in Fig. 2. It is apparent that the amounts of \( CO \) and \( O_2 \) decrease while that of \( CO_2 \) increases. That is, \( CO \) and \( O_2 \), which are the reactants, react to form \( CO_2 \), which is the product, in the reactor. Since the amount of \( CO_2 \) increases along the reactor, the reaction must be governed by the chemical equation

\[
CO + \frac{1}{2} O_2 \rightarrow CO_2
\]

which states that, for the production of 1 kmol of \( CO_2 \), 1 kmol of \( CO \) and 0.5 kmol of \( O_2 \) must be consumed.

Along the reactor, the decrease of the amounts of \( CO \) and \( O_2 \) and the increase...
of the amount of CO₂ are analogous to the heat loss by the hot water and the heat gain by the cold water in the thermal reactor above. Downstream of station 3, the composition of the mixture remains constant: with about 2.9 kmol of CO, 1.95 kmol of O₂, and 4.1 kmol of CO₂ (to be verified later in Example 1). We say now that a chemical equilibrium has been reached, much like the thermal equilibrium condition attained by the hot and cold water streams in the thermal reactor above.

Let us now consider 2 kmol of CO, 1.5 kmol of O₂, and 5 kmol of CO₂ entering the same chemical reactor at 3,000 K and 1 atm. If we could again monitor the amounts of CO, O₂, and CO₂ along the reactor, it could be shown that the amounts of CO and O₂ increase while that of CO₂ decreases along the reactor. That is, CO₂ decomposes to form CO and O₂ in the reactor. Thus, the reaction is the reverse of that given by eq. (1) above.

\[ CO₂ \rightarrow CO + \frac{1}{2} O₂ \]  

(2)

One kilomole of CO₂ must be consumed to produce 1 kmol of CO and 0.5 kmol of O₂. The mixture attains a chemical equilibrium when the mixture consists of about 2.9 kmol of CO, 1.95 kmol of O₂, and 4.1 kmol of CO₂. Therefore, the direction of the chemical reaction appears to be dependent on the relative amounts of the gases entering the reactor at given temperature and pressure.

Next, we consider the following chemical reaction under atmospheric conditions

\[ \frac{1}{2} N₂ + \frac{1}{2} O₂ \rightarrow NO \]  

(3)

If the complete reaction had occurred, consuming all the oxygen, since the earth was created, our ancestors would have laughed after inhaling the nitric oxide gas and would have died later for the lack of oxygen. Fortunately, the oxidation of nitrogen to form nitric oxide does not go to completion at ambient temperature and pressure, and the reaction stops when a chemical equilibrium is reached.

We are familiar with the thermophysical property temperature. We also know that heat flows in the direction of decreasing temperature and that systems are in thermal equilibrium when their temperatures are equal. Is it possible to define a property that is analogous to thermal potential or temperature, the relative amount of which determines the direction of a chemical reaction? Let us assume that there is such a property and let us call it "reaction potential," or, loosely as "reaction temperature." It may be possible to define reaction temperature such that the value of the reaction temperature of the reactants is always larger than that of the products in a chemical reaction. In the first case of 5 kmol of CO, 3 kmol of O₂, and 2 kmol of CO₂ entering the chemical reactor above, the oxidation of CO may be predicted by comparing the
reaction temperature of CO and O\textsubscript{2} with that of CO\textsubscript{2} at the reactor inlets. The direction of the reaction, given by eq. (1), may be the result of the higher reaction temperature of CO and O\textsubscript{2} than that of CO\textsubscript{2} at the reactor inlets. In the second case of 2 kmol of CO, 1.5 kmol of O\textsubscript{2}, and 5 kmol of CO\textsubscript{2} entering the chemical reactor above, the decomposition of CO\textsubscript{2} may be due to the higher reaction temperature of CO\textsubscript{2} and the lower reaction temperature of CO and O\textsubscript{2} at the reactor inlets.

Is it also possible to define reaction temperature such that, as a system approaches a chemical equilibrium, the reaction temperature of the reactants decreases and that of the products increases? Using the chemical reactor examples above, after the mixture of CO\textsubscript{2}, O\textsubscript{2}, and CO\textsubscript{2} attains a chemical equilibrium, can the reaction temperature of CO and O\textsubscript{2} be equal to that of CO\textsubscript{2} and remain constant thereafter (similar to the constant temperature in a system once a thermal equilibrium is attained)? Also, can the equilibrium composition of the CO, O\textsubscript{2}, and CO\textsubscript{2} mixture be predicted by setting the reaction temperature of CO and O\textsubscript{2} equal to that of CO\textsubscript{2}, which is equivalent to the prediction of thermal equilibrium conditions using the First Law of Thermodynamics?

The Second Law provides the answers. We know that heat transfer is in the direction of decreasing temperature and is irreversible. When heat transfer takes place, entropy is produced. Since a chemical reaction is also irreversible, the reaction must proceed in a direction that leads to the production of entropy.

**Analysis**

In this section, we first present the criterion that governs the direction of a chemical reaction. We then define reaction temperature and proceed to demonstrate how reaction temperature determines the direction of a chemical reaction and the equilibrium composition of a gaseous mixture.

**Direction of Chemical Reaction and Equilibrium Criterion**

For a simple compressible system undergoing an irreversible process, energy and entropy balances give

\[ \delta Q = dU + \delta W \]  

(4)

and

\[ dS = \frac{\delta Q}{T} + \delta \sigma \]  

(5)


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If only compressible work is considered and the process takes place at constant temperature and pressure, it has been shown in conventional thermodynamics texts [1-6], by using eqs. (4) and (5), that

$$dG |_{T,p} = -T \delta \sigma$$

(6)

where $G$ is the Gibbs function of the system and is defined as $H - TS$. Since $\delta \sigma$ is always greater than zero, the Gibbs function of a system decreases during an irreversible process. When the system attains an equilibrium or a reversible state, $\delta \sigma = 0$, and the Gibbs function of the system has a minimum value. That is,

$$dG |_{T,p} = 0$$

(7)

For a multicomponent ideal gas mixture,

$$G = \sum n_i \bar{h}_i(T) - T \sum n_i \bar{s}_i(T,p_i)$$

(8)

where $n_i$, $\bar{h}_i(T)$, $\bar{s}_i(T,p_i)$, and $p_i$ are the number of moles, the specific enthalpy, the specific entropy, and the partial pressure of component $i$ in the mixture. Differentiating eq. (8),

$$dG = \sum dn_i \bar{h}_i(T) + \sum n_id\bar{h}_i(T) - T \sum dn_i \bar{s}_i(T,p_i) - T \sum n_id\bar{s}_i(T,p_i)$$

(9)

Since the temperature is constant, the second term on the right side of eq. (9) is equal to zero. Using $\bar{s}_i(T,p_i) = \bar{s}^\circ_i(T,p_{ref}) - \bar{R} \ln \left( \frac{y_i p}{p_{ref}} \right)$ to rewrite the last term in eq. (9) with pressure constant,

$$- T \sum n_i d\bar{s}_i(T,p_i) = n\bar{R}T \left( \frac{p_{ref}}{p} \right) \sum dy_i = 0$$

(10)

Thus, equation (9) may be simplified to

$$dG = \sum dn_i \bar{h}_i(T) - T \sum n_i \bar{s}_i(T,p_i)$$

(11)

Defining the partial molal Gibbs function of component $i$ (which is the same as the chemical potential of component $i$ in an ideal gas mixture) as
\[ \bar{g}_i(T,p_i) = \bar{h}_i(T) - T\bar{s}_i(T,p_i) \]

\[ = \bar{h}_i(T) - T\bar{s}^{o}_i(T,p_{\text{ref}}) + \bar{R}T \ln \left( \frac{p_i}{p_{\text{ref}}} \right) \] (12)

Equation (6) becomes

\[ \sum d_n \bar{g}_i(T,p_i) = -T \delta \sigma \] (13)

It should be noted that the partial molal Gibbs function of a species in an ideal gas mixture increases with increasing partial pressure, that is, as the population of the species increases. Also, although an ideal gas mixture is assumed throughout the derivation, the equilibrium criterion in terms of the Gibbs function is applicable to mixtures of real gases and liquids in general.

Similarly, it may be shown that eq. (13) is also applicable to a simple compressible system that undergoes an irreversible process at constant temperature and volume (for instance, an isothermal process that takes place in a rigid closed vessel).

**Reaction Temperature**

**Oxidation of Carbon Monoxide** In the case of 5 kmol of CO, 3 kmol of O₂, and 2 kmol of CO₂ entering the chemical reactor above, let us assume that the direction of the reaction is given as in eq. (1). If \( dn_{CO} = -0.001 \) kmol, \( dn_{O_2} = -0.0005 \) kmol and \( dn_{CO_2} = 0.001 \) kmol. Equation (13) becomes

\[ (-0.001) \bar{g}_{CO}(T,p_{CO}) + (-0.0005) \bar{g}_{O_2}(T,p_{O_2}) \]

\[ + (0.001) \bar{g}_{CO_2}(T,p_{CO_2}) = -T \delta \sigma \] (14)

Dividing eq. (14) by - 0.001, we get

\[ \bar{g}_{CO}(T,p_{CO}) + (1/2) \bar{g}_{O_2}(T,p_{O_2}) - \bar{g}_{CO_2}(T,p_{CO_2}) = T \sigma \] (15)

The term \( \sigma \) on the right side of eq. (15) represents the entropy generated when 1 kmol of CO is consumed during the reaction. The left side of eq. (15) is known as the affinity of the reaction. Since \( \sigma > 0 \), affinity is always greater than zero.

Rearranging eq. (15), we get
\[ \bar{g}_{\text{CO}}(T, p_{\text{CO}}) + \frac{1}{2} \bar{g}_{\text{O}_2}(T, p_{\text{O}_2}) > \bar{g}_{\text{CO}_2}(T, p_{\text{CO}_2}) \]  

(16)

The coefficients in eq. (16) are the stoichiometric coefficients in eq. (1). Indeed, we can show that the left side of eq. (16) is greater than the right side by evaluating the partial molal Gibbs functions at the inlet conditions. Thus, the direction of the reaction is given as in eq. (1).

Now, let us define the reaction temperature of the reactants, CO and O\(_2\), as

\[ T_{\text{react, CO} \cdot \text{O}_2} = \bar{g}_{\text{CO}}(T, p_{\text{CO}}) + \frac{1}{2} \bar{g}_{\text{O}_2}(T, p_{\text{O}_2}) \]  

(17)

and that of the product, CO\(_2\), as

\[ T_{\text{react, CO}_2} = \bar{g}_{\text{CO}_2}(T, p_{\text{CO}_2}) \]  

(18)

Then, at the inlet,

\[ T_{\text{react, CO} \cdot \text{O}_2} > T_{\text{react, CO}_2} \]  

(19)

Along the reactor, the amounts of CO and O\(_2\) decrease, with a corresponding increase in the amount of CO\(_2\). When the populations of CO and O\(_2\) decrease, the partial molal Gibbs functions decrease [see eq. (12)]. As a result, the reaction temperature of the reactants, CO and O\(_2\), drops. At the same time, the partial molal Gibbs function of CO\(_2\) increases, raising the reaction temperature of CO\(_2\). Eventually, the reaction temperature of CO and O\(_2\) equals that of CO\(_2\) and we say that a chemical equilibrium is reached.

\[ T_{\text{react, CO} \cdot \text{O}_2} = T_{\text{react, CO}_2} \]  

(20)

Further downstream, the composition of the equilibrium gaseous mixture remains constant. No further reaction takes place, as there is no difference between the reaction temperature of CO and O\(_2\) and that of CO\(_2\). Thus, the chemical reaction proceeds in the direction of decreasing reaction temperature, in the same manner as the flow of heat in the direction of decreasing temperature. The chemical reaction stops when the reaction temperature of the reactants and that of the products are equal, which is analogous to the absence of heat transfer between two media at the same temperature.

**General Chemical Reaction** Let us generalize the definitions of the reaction temperatures of the reactants and the products of any chemical reaction and the
relationship between them. Consider the following chemical reaction that takes place at constant temperature and pressure in an ideal gas mixture consisting of four components, A, B, C, and D:

\[ \alpha_A A + \alpha_B B \rightarrow \alpha_C C + \alpha_D D \]  

(21)

where A and B are the reactants, C and D are the products, and the \( \alpha \)'s are the stoichiometric coefficients. If we define the reaction temperature of the reactants as

\[ T_{\text{react, } A + B} = \alpha_A \overline{s}_A + \alpha_B \overline{s}_B \]  

(22)

and that of the products as

\[ T_{\text{react, } C + D} = \alpha_C \overline{s}_C + \alpha_D \overline{s}_D \]  

(23)

the equilibrium criterion for the reaction given by eq. (21) is

\[ T_{\text{react, } A + B} \geq T_{\text{react, } C + D} \]  

(24)

Note that the unit for reaction temperature is kJ, not degrees Kelvin. Thus, the reaction temperature of the reactants, A and B, is always higher than or equal to that of the products, C and D. The direction of the chemical reaction must be such that A and B, at a higher reaction temperature, combine to form C and D, at a lower reaction temperature. As the reaction proceeds toward an equilibrium state, the amounts of A and B in the mixture decrease, lowering their reaction temperature, while the amounts of C and D increase, raising their reaction temperature. At equilibrium, the reaction temperature of A and B is equal to that of C and D, and we may say that the tendency of A and B combining to form C and D is balanced by the tendency of C and D combining to form A and B.

**Examples**

The following examples illustrate how reaction temperature may be used to determine the direction of a chemical reaction and the composition of an equilibrium gaseous mixture:

**Example 1**

Consider the case of 5 kmol of CO, 3 kmol of O\(_2\), and 2 kmol of CO\(_2\) entering
a chemical reactor at 3,000 K and 1 atm, as shown schematically in Fig. 2. The temperature and pressure are maintained constant along the reactor.

**Reaction Temperature Approach** Using eqs. (12), (17), and (18), with $p_{CO} = 0.5$ atm, $p_{O_2} = 0.3$ atm, and $p_{CO_2} = 0.2$ atm, the reaction temperature of CO and O$_2$ and that of CO$_2$ at the inlets are evaluated as $-1.248 \times 10^6$ kJ and $-1.283 \times 10^6$ kJ, respectively. Since the reaction temperature of CO and O$_2$ is higher than that of CO$_2$, CO and O$_2$ react to form CO$_2$, and the amount of CO$_2$ increases along the reactor. A spreadsheet computer software was used to calculate the values of the reaction temperatures for given amounts of CO$_2$, taking into account the corresponding decreases of the amounts (and the partial pressures) of CO and O$_2$ as the amount (and the partial pressure) of CO$_2$ increases. For instance, at a station (2) where there are 3 kmol of CO$_2$, 1 kmol of CO$_2$ has been produced after 1 kmol of CO has reacted with $\frac{1}{2}$ kmol of O$_2$. Therefore, at station (2), there are 4 kmol of CO, 2$\frac{1}{2}$ kmol of O$_2$, and 3 kmol of CO$_2$. The partial pressures of CO, O$_2$, and CO$_2$ are 0.421, 0.263, and 0.316 atm, respectively. From the values of the partial pressures, the reaction temperature of CO and O$_2$ and that of CO$_2$ at station (2) are then evaluated as $-1.253 \times 10^6$ kJ and $-1.272 \times 10^6$ kJ, respectively.

Figure 3 shows the reaction temperature of CO and O$_2$ and that of CO$_2$ as functions of the number of moles of CO$_2$ in the gaseous mixture as the mixture flows through the reactor. At station (3), the two reaction temperatures are equal, indicating that a chemical equilibrium is reached. To determine the composition of the equilibrium mixture, we set the reaction temperature of CO and O$_2$ equal to that of CO$_2$. Thus,

$$\vec{g}_{CO}(T,p_{CO}) + \frac{1}{2} \vec{g}_{O_2}(T,p_{O_2}) = \vec{g}_{CO_2}(T,p_{CO_2})$$

(25)

where $\vec{g}_i(T,p_i)$ of each component $i$ is dependent on the partial pressure of component $i$ [see eq. (12)], that is, the mole fraction. Since

$$5CO + 3O_2 + 2CO_2 \rightarrow n_{CO}CO + n_{O_2}O_2 + n_{CO_2}CO_2$$

(26)

and the total numbers of carbon and oxygen atoms entering the reactor must be equal to those in the equilibrium mixture,

$$n_{CO} + n_{CO_2} = 5 + 2 = 7$$

(27)
a chemical reactor at 3,000 K and 1 atm, as shown schematically in Fig. 2. The
temperature and pressure are maintained constant along the reactor.

**Reaction Temperature Approach**

Using eqs. (12), (17), and (18), with $p_{CO} = 0.5$
atm, $p_{O_2} = 0.3$ atm, and $p_{CO_2} = 0.2$ atm, the reaction temperature of CO and O$_2$ and
that of CO$_2$ at the inlets are evaluated as $- 1.248 \times 10^6$ kJ and $- 1.283 \times 10^6$ kJ,
respectively. Since the reaction temperature of CO and O$_2$ is higher than that of CO$_2$,
CO and O$_2$ react to form CO$_2$, and the amount of CO$_2$ increases along the reactor. A
spreadsheet computer software was used to calculate the values of the reaction
temperatures for given amounts of CO$_2$, taking into account the corresponding decreases
of the amounts (and the partial pressures) of CO and O$_2$ as the amount (and the partial
pressure) of CO$_2$ increases. For instance, at a station (2) where there are 3 kmol of
CO$_2$, 1 kmol of CO$_2$ has been produced after 1 kmol of CO has reacted with $1/2$ kmol
of O$_2$. Therefore, at station (2), there are 4 kmol of CO, $21/2$ kmol of O$_2$, and 3 kmol
of CO$_2$. The partial pressures of CO, O$_2$, and CO$_2$ are 0.421, 0.263, and 0.316 atm,
respectively. From the values of the partial pressures, the reaction temperature of CO
and O$_2$ and that of CO$_2$ at station (2) are then evaluated as $-1.253 \times 10^6$ kJ and $- 1.272$
x $10^6$ kJ, respectively.

Figure 3 shows the reaction temperature of CO and O$_2$ and that of CO$_2$ as
functions of the number of moles of CO$_2$ in the gaseous mixture as the mixture flows
through the reactor. At station (3), the two reaction temperatures are equal, indicating
that a chemical equilibrium is reached. To determine the composition of the
equilibrium mixture, we set the reaction temperature of CO and O$_2$ equal to that of
CO$_2$. Thus,

$$\bar{\xi}_{CO}(T,p_{CO}) + \frac{1}{2} \bar{\xi}_{O_2}(T,p_{O_2}) = \bar{\xi}_{CO_2}(T,p_{CO_2}) \quad (25)$$

where $\bar{\xi}_i(T,p_i)$ of each component $i$ is dependent on the partial pressure of component
$i$ [see eq. (12)], that is, the mole fraction. Since

$$5\text{CO} + 3\text{O}_2 + 2\text{CO}_2 \rightarrow n_{CO}\text{CO} + n_{O_2}\text{O}_2 + n_{CO_2}\text{CO}_2 \quad (26)$$

and the total numbers of carbon and oxygen atoms entering the reactor must be equal
to those in the equilibrium mixture,

$$n_{CO} + n_{CO_2} = 5 + 2 = 7 \quad (27)$$
\[ n_{\text{CO}} + 2n_{\text{O}_2} + 2n_{\text{CO}_2} = 5 + 3(2) + 3(2) = 15 \] (28)

Expressing \( n_{\text{CO}} \) and \( n_{\text{O}_2} \) in terms of \( n_{\text{CO}_2} \) and replacing the partial pressure in \( \bar{g}_i(T, p_i) \) of each component \( i \) with the corresponding mole fraction, eq. (25) may be solved with a simple computer program and an appropriate software for thermodynamic properties to get \( n_{\text{CO}_2} = 4.112 \text{ kmol} \). Thus, the equilibrium mixture consists of 2.888 kmol of CO, 1.944 kmol of O\(_2\), and 4.112 kmol of CO\(_2\).

Alternatively, one may simply use Fig. 3 along with eqs. (27) and (28) to obtain the composition of the equilibrium mixture. Figure 3 indicates that the two reaction temperature distributions intersect when there is 4.112 kmol of CO\(_2\) in the mixture.

Beyond station (3), the reaction temperature of CO and O\(_2\) could drop to below that of CO\(_2\), if CO and O\(_2\) were to continue to react to form CO\(_2\). That would have caused the Gibbs function of the system to increase, which would violate the equilibrium criterion, eq. (6). Once a chemical equilibrium is reached, the composition of the mixture, and thus, the reaction temperatures, must remain unchanged. Figure 4 gives the total Gibbs function of the system, \( G = n_{\text{CO}} \bar{g}_{\text{CO}}(T, p_{\text{CO}}) + n_{\text{O}_2} \bar{g}_{\text{O}_2}(T, p_{\text{O}_2}) + n_{\text{CO}_2} \bar{g}_{\text{CO}_2}(T, p_{\text{CO}_2}) \), as the amount of CO\(_2\) in the system increases. The Gibbs function distribution has a minimum at station (3) when \( n_{\text{CO}_2} = 4.112 \text{ kmol} \). Therefore, in the actual system, the reaction temperature distributions in Fig. 3 should end at station (3).

**Classical Solution** To determine the composition of the equilibrium mixture in the classical manner, we express the partial molal Gibbs function of each component in eq. (25) in terms of the corresponding molal Gibbs function evaluated at \( T \) and the reference pressure of 1 atm,

\[
\left[ \bar{g}_{\text{CO}}(T, p_{\text{ref}}) + RT \ln \left( \frac{p_{\text{CO}}}{p_{\text{ref}}} \right) \right] + \frac{1}{2} \left[ \bar{g}_{\text{O}_2}(T, p_{\text{ref}}) + RT \ln \left( \frac{p_{\text{O}_2}}{p_{\text{ref}}} \right) \right] = \left[ \bar{g}_{\text{CO}_2}(T, p_{\text{ref}}) + RT \ln \left( \frac{p_{\text{CO}_2}}{p_{\text{ref}}} \right) \right]
\]

(29)

By introducing \( \Delta G^\circ = \bar{g}_{\text{CO}_2}(T, p_{\text{ref}}) - \bar{g}_{\text{CO}}(T, p_{\text{ref}}) - \frac{1}{2} \bar{g}_{\text{O}_2}(T, p_{\text{ref}}) \) and replacing the pressure ratios with the corresponding mole fractions, eq. (29) becomes

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\[
\frac{\left(\frac{p_{CO_2}}{p_{\text{ref}}}ight)}{\left(\frac{p_{CO}}{p_{\text{ref}}}ight)^{1/2}} = \frac{\left(\frac{n_{CO_2}}{n}\right)}{\left(\frac{n_{CO}}{n}\right)^{1/2}} \left(\frac{p}{p_{\text{ref}}^{1/2}}\right)^{-1/2}
\]

\[
= \exp\left(-\frac{\Delta G^e}{RT}\right) = K
\]  

(30)

where the total number of moles of the mixture, \(n\), is the sum of \(n_{CO}\), \(n_{O_2}\), and \(n_{CO_2}\), and \(K\) is the equilibrium constant. With the appropriate values of \(\bar{h}(T)\) and \(\bar{s}^o(T, p_{\text{ref}})\), and \(T = 3,000\) K, it may be shown that \(K = 3.055\).

Solving eqs. (27), (28), and (30), the equilibrium composition with 2.888 kmol of CO, 1.944 kmol of O\(_2\), and 4.112 kmol of CO\(_2\) is again obtained.

**Example 2**

Consider the case of 2 kmol of CO, 1.5 kmol of O\(_2\), and 5 kmol of CO\(_2\) entering a chemical reactor at 3,000 K and 1 atm. Figure 5 shows the reaction temperature of CO and O\(_2\) and that of CO\(_2\) as functions of the number of moles of CO\(_2\) in the gaseous mixture as the mixture flows through the reactor. Since the reaction temperature of CO\(_2\) is higher than that of CO and O\(_2\) at the inlets, CO\(_2\) decomposes to form CO and O\(_2\), and the amount of CO\(_2\) decreases along the reactor. That is, the reaction follows eq. (2).

The reaction temperature of CO and O\(_2\) increases and that of CO\(_2\) decreases as the mixture flows through the reactor. The two reaction temperatures attain a constant value at station (3) after a chemical equilibrium is reached. Since the total numbers of carbon and oxygen atoms entering the reactor are the same as those entering the reactor in Example 1, and the temperature and pressure are the same as those in Example 1, the equilibrium mixture must also consist of 2.888 kmol of CO, 1.944 kmol of O\(_2\), and 4.112 kmol of CO\(_2\).

**Example 3**

Let us determine the trace amount of nitric oxide (NO) in atmospheric air, if air is assumed to be in chemical equilibrium. For NO to exist in equilibrium with N\(_2\) and O\(_2\) in air, the reaction temperature of N\(_2\) and O\(_2\) must be equal to that of NO.
\[ T_{\text{react, } N_2 \cdot O_2} = T_{\text{react, } NO} \] (31)

or,

\[ \frac{1}{2} \bar{g}_{N_2}(298K, p_{N_2}) + \frac{1}{2} \bar{g}_{O_2}(298K, p_{O_2}) = \bar{g}_{NO}(298K, p_{NO}) \] (32)

Since the partial pressures of N\(_2\) and O\(_2\) in atmospheric air are not affected significantly by the presence of a trace amount of NO, \( p_{N_2} \approx 0.79 \) atm, \( p_{O_2} \approx 0.21 \) atm, and \( p_{NO} = y_{NO} \) atm. Equation (32) may be rewritten with eq. (12) in terms of the appropriate values of specific enthalpy and specific entropy, and the partial pressures. The resulting equation may then be solved for the only unknown, \( p_{NO} \), in the equation. With \( p_{NO} = y_{NO} \) atm, one gets

\[ y_{NO} = 2.75 \times 10^{-16} \]

which is an extremely small quantity. It may be shown that, if the temperature of air is raised to 3,000 K, the mole fraction of nitric oxide in air is about 0.05. Thus, nitrogen and oxygen react more readily at higher temperatures to produce nitric oxide, and there is much more than just a trace amount of nitric oxide in air at high temperatures.

**Conclusion**

This paper presents the concept of reaction temperature to help students understand chemical equilibrium in their thermodynamics classes. The definition of reaction temperature is derived from the observation that a chemical reaction toward an equilibrium state is analogous to heat transfer in an isolated medium until the medium attains a uniform temperature, and from the fact that a chemical reaction is irreversible and results in the production of entropy. The reaction temperature of the reactants is always higher than that of the products. As a chemical reaction proceeds toward an equilibrium state, the reaction temperature of the reactants decreases and that of the products increases. At equilibrium, the reaction temperatures of the reactants and the products are the same. This paper gives examples to show how reaction temperature is used to determine the direction of a chemical reaction toward an equilibrium state and the composition of the equilibrium mixture. In this paper, only examples for simple chemical reactions are given. The procedure was also extended to deal with complicated simultaneous reactions by equating the reaction temperatures of the reactants and products of each reaction. To keep this paper a reasonable length, the results for simultaneous reactions are not presented here.
References

Fig. 1. Temperature distributions of hot and cold water streams in a long, well-insulated, parallel flow heat exchanger.
<table>
<thead>
<tr>
<th>Station 1 (Inlet)</th>
<th>Station 2</th>
<th>Station 3</th>
<th>Station 4 (Exit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{CO} = 5 \text{ kmol} )</td>
<td>( n_{CO} = 4 \text{ kmol} )</td>
<td>( n_{CO} = 2.9 \text{ kmol} )</td>
<td>( n_{CO} = 2.9 \text{ kmol} )</td>
</tr>
<tr>
<td>( n_{O_2} = 3 \text{ kmol} )</td>
<td>( n_{O_2} = 2.5 \text{ kmol} )</td>
<td>( n_{O_2} = 1.95 \text{ kmol} )</td>
<td>( n_{O_2} = 1.95 \text{ kmol} )</td>
</tr>
<tr>
<td>( n_{CO_2} = 2 \text{ kmol} )</td>
<td>( n_{CO_2} = 3 \text{ kmol} )</td>
<td>( n_{CO_2} = 4.1 \text{ kmol} )</td>
<td>( n_{CO_2} = 4.1 \text{ kmol} )</td>
</tr>
</tbody>
</table>

\[ T = 3,000 \text{ K} \quad p = 1 \text{ atm} \]

Fig. 2. Composition of mixture of \( \text{CO}, \text{O}_2, \) and \( \text{CO}_2 \) at various stations in a chemical reactor.
Fig. 3. Reaction temperatures of reactants (CO and O₂) and product (CO₂) for \( CO + \frac{1}{2} O₂ → CO₂ \) as functions of amount of CO₂ in mixture.
Fig. 4. Variation of total Gibbs function for \( CO + \frac{1}{2}O_2 \rightarrow CO_2 \) with amount of \( CO_2 \) in mixture.
Fig. 5. Reaction temperatures of reactant (CO₂) and products (CO and O₂) for $CO_2 \rightarrow CO + \frac{1}{2}O_2$ as functions of amount of CO₂ in mixture.