KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY
CHEMICAL ENGINEERING DEPARTMENT
CHE 252: CHEMICAL PROCESS CALCULATIONS II
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LECTURE 6: ENERGY BALANCE ON NON REACTIVE PROCESSES (II)

Learning Objectives

At the end of this lecture the students will learn how to calculate internal energy and enthalpy changes associated with the following type of processes as well as performing energy balances on such processes:

1. Changes in P at constant T and state of aggregation (isothermal changes in pressure).

2. Changes in T at constant P and state of aggregation (isobaric changes in temperature).

3. Phase changes at constant T and P-melting, solidifying, vaporizing, condensing, and sublimating (isothermal isobaric phase change).

4. Mixing of two liquids or dissolving of a gas or a solid in a liquid at constant T and P (isothermal isobaric mixing of two or more species).

Students are expected to understand the variables *Cv(T)* (heat capacity at constant volume), C*p(T)* (heat capacity at constant pressure), $\Delta \widehat{H}_m$ (heat of fusion or heat of melting), $\Delta \widehat{H}_v$ (heat of vaporization), standard heats of fusion and vaporization, and $\Delta \widehat{H}_s$ (heat of solution or heat of mixing).

6.1 Introduction

This lecture presents procedures for evaluating $\Delta \dot{H}$ or $\Delta \dot{U}$ when tables of $\widehat{H}$ and $\widehat{U}$ are not available for all process species. Once these calculations have been performed, the energy balance may be written and solved as before.

6.2 Changes in Pressure at Constant Temperature

It has been observed experimentally that internal energy is nearly independent of pressure for solids and liquids at a fixed temperature, as is specific volume. Therefore, *if the pressure of a solid or liquid changes at constant temperature, you may write* $\Delta \widehat{U} \approx 0 \; and \; \Delta \widehat{H} \left[= \Delta \widehat{U} + \Delta \left(P\widehat{V} \right) \right] \approx \widehat{V} \Delta P.$

Both $\widehat{U}$ and $\widehat{H}$ are independent of pressure for ideal gases. Consequently, *you may generally assume $\Delta\widehat{U} \approx 0$ and $\Delta\widehat{H} \approx 0$ for a gas undergoing an isothermal pressure change unless gases at temperatures well below 0°C or well above 1 atm are involved.* [If tables of $\widehat{U}(T,P)$ or $\widehat{H}(T,P)$ are available for the gas, there is of course no need to make this assumption.]

If gases are far from ideal or if they undergo large pressure changes, you must either use tables of thermodynamic properties (such as the steam tables for water) or thermodynamic correlations to determine $\Delta\widehat{U}$ *and* $\Delta\widehat{H}$.

6.3 Changes in Temperature

### 6.3.1 Sensible Heat and Heat Capacities

The term sensible heat signifies heat that must be transferred to raise or lower the temperature of a substance or mixture of substances. The quantity of heat required to produce a temperature change in a system can be determined from the appropriate form of the first law of thermodynamics:

$$Q = \Delta U \text{ (closed system)}$$
$$\dot{Q} = \Delta\dot{H} \text{ (open system)}$$

(Kinetic and potential energy changes and work have been neglected). To determine the sensible heat requirement for a heating or cooling process, you must therefore be able to determine ΔU or $\Delta\dot{H}$ for the specified temperature change.

The specific internal energy of a substance depends strongly on temperature. If the temperature is raised or lowered in such a way that the system volume remains constant, the specific internal energy might vary as shown in the following plot:
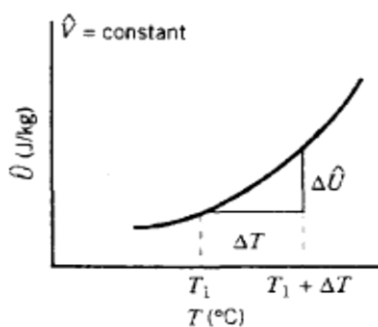
A temperature change ΔT from T_1 leads to a change $\Delta\widehat{U}$ in specific internal energy. As $\Delta T \rightarrow 0$, the ratio $\Delta\widehat{U}/\Delta T$ approaches a limiting value (i.e., the slope of the curve at T_1) which is by definition **the heat capacity at constant volume** of the substance, denoted by **Cv** .

$$C_v(T) = \left\{\lim_{\Delta T \rightarrow 0} \frac{\Delta\widehat{U}}{\Delta T}\right\} = \left(\frac{\partial\widehat{U}}{\partial T}\right)_v$$

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Since the plot of $\hat{U}$ versus T is not generally a straight line, C_v (the slope of the curve) is a function of temperature.

The change in $\hat{U}$ for a temperature rise from T to $T + dT$ at constant volume is

$$d\hat{U} = C_v(T)dT$$

and the change $\Delta\hat{U} = \hat{U}_2 - \hat{U}_1$ associated with a temperature change from T_1 to T_2 at constant volume is, accordingly,

$$\Delta\hat{U} = \int_{T_1}^{T_2} C_v(T)dT$$

Now, suppose both the temperature and the volume of a substance change. To calculate $\Delta\hat{U}$ you may break the process into two steps-a change in V at constant T followed by a change in T at constant V.

$$A(T_1, \hat{V}_1) \xrightarrow{\Delta\hat{U}_1} A(T_1, \hat{V}_2) \xrightarrow{\Delta\hat{U}_2} A(T_2, \hat{V}_2)$$

$$\Delta\hat{U}$$
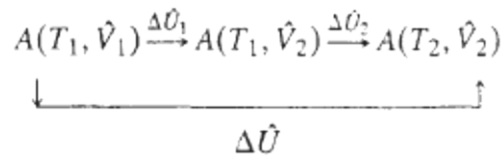
Since $\hat{U}$ is a state property, $\Delta\hat{U}$ (the desired quantity) equals $\Delta\hat{U}_1 + \Delta\hat{U}_2$. But for ideal gases and (to a good approximation) liquids and solids, $\hat{U}$ depends only on T, so that since T is constant in step 1, $\Delta\hat{U}_1 = 0$ for any substance but a non-ideal gas. Moreover, since the second step is a change in temperature at constant volume, $\Delta\hat{U}_2$ is given by

$$\Delta\hat{U} = \int_{T_1}^{T_2} C_v(T)dT$$

In summary, then, for a temperature change from T_1 to T_2

$$\Delta\hat{U} \approx \int_{T_1}^{T_2} C_v(T)dT$$

Comments: Ideal gas: *exact*

Solid or liquid: *good approximation*

Non-ideal gas: *valid only if V is constant*

Example 6.1 *Evaluation of an Internal Energy Change from Tabulated Heat Capacity*

Calculate the heat required to raise 200 kg of nitrous oxide from 20°C to 150°C in a constant-volume vessel. The constant-volume heat capacity of N_2O in this temperature range is given by the equation

$$C_v(\text{kJ/kg.°C}) = 0.855 + 9.42 \times 10^{-4}T$$

where T is in ºC.

Solution

$$\Delta \hat{U} \approx \int_{T_1}^{T_2} C_v(T) dT$$

$$\Delta \hat{U}(kJ/kg) = \int_{20°C}^{150°C} (0.855 + 9.42 \times 10^{-4}T) \left(\frac{kJ}{kg.°C}\right) dT$$

$$= 0.855T]_{20°C}^{150°C} + \frac{9.42 \times 10^{-4}T^2}{2}\Bigg]_{20°C}^{150°C}$$

$$= (111 + 10.4) \, kJ/kg = 121 \, kJ/kg$$

The energy balance for this closed system is

$$Q = \Delta U = m \, (kg)\Delta\hat{U}(kJ/kg) = 200 \, kg \times 121 \, kJ/kg = 24200 \, kJ$$

Heat capacity at constant pressure

Next, let us suppose that we heat a substance at constant pressure and consider the resulting change in enthalpy. Like internal energy, enthalpy depends strongly on temperature. If $\Delta\hat{H}$ is the change in specific enthalpy resulting from a temperature increase at constant pressure from T to $T + \Delta T$, then as ΔT approaches zero the ratio $\Delta\hat{H}/\Delta T$ approaches a limiting value, defined as the **heat capacity at constant pressure** and denoted by C_p

$$C_p(T) = \left\{\lim_{\Delta T \to 0} \frac{\Delta\hat{H}}{\Delta T}\right\} = \left(\frac{\partial\hat{H}}{\partial T}\right)_P$$
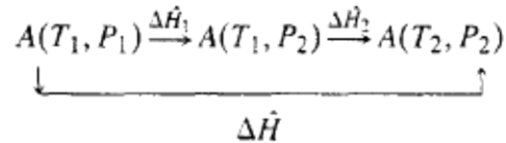
Proceeding as before, we observe that the change in $\hat{H}$ for a temperature change at constant pressure from T to $T + dT$ is

$$d\hat{H} = C_p(T)dT$$

and so for a change from T_1 to T_2 at constant pressure,

$$\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T) dT$$

For a process $A(T_1, P_1) \to A(T_2, P_2)$, we may construct a two-step process path

$$A(T_1, P_1) \xrightarrow{\Delta \hat{H}_1} A(T_1, P_2) \xrightarrow{\Delta \hat{H}_2} A(T_2, P_2)$$

$$\underbrace{\phantom{A(T_1, P_1) \xrightarrow{\Delta \hat{H}_1} A(T_1, P_2) \xrightarrow{\Delta \hat{H}_2} A(T_2, P_2)}}_{\Delta \hat{H}}$$

The first step is a change in pressure at constant temperature

$$\Delta \hat{H}_1 = 0 \text{ (Ideal gas)}$$
$$\Delta \hat{H}_1 = \hat{V} \Delta P \text{ (solid or liquid)}$$

The second step is a change in temperature at constant pressure, so that $\Delta \hat{H}_2$ is given by

$$\Delta \hat{H} = \int_{T_1}^{T_2} C_p(T) dT$$

Finally, since $\Delta H = \Delta \hat{H}_1 + \Delta \hat{H}_2$, we obtain

$$\boxed{\Delta \hat{H} = \int_{T_1}^{T_2} C_p(T)\, dT} \qquad \begin{array}{l}\text{Ideal gas: exact} \\ \text{Nonideal gas: exact only if } P \text{ is constant}\end{array}$$

$$\boxed{\Delta \hat{H} = \hat{V}\, \Delta P + \int_{T_1}^{T_2} C_p(T)\, dT} \qquad \text{Solid or liquid}$$

For all but large pressure changes and small temperature changes, the first term of the last equation above, $\hat{V} \Delta P$, is usually negligible relative to the second term.

Evaluating $\Delta \hat{H}$ for a nonideal gas undergoing a temperature and pressure change is best done using tabulated enthalpies. If none are available, a thermodynamic relation for variations of H with P must be combined with this equation to determine the enthalpy change:

$$\Delta \hat{H} = \int_{T_1}^{T_2} C_p(T) dT$$

6.3.2 Heat Capacity Formulas
The heat capacities C_v and C_p (*specific heat*) are physical properties of materials and are tabulated in standard references such as Perry's Chemical Engineer's Handbook. They may be expressed in any units of energy per unit amount per unit temperature interval e.g. J/(mol.K) or Btu/(Ib$_m$.°F). Heat capacities are functions of temperature and are frequently expressed in polynomial form ($C_p = a + bT + cT^2 + dT^3$).

Simple relationships exists between C_p and C_v in two cases:
   a) *Liquids and Solids: $C_p \approx C_v$*

b) **Ideal Gases: $Cp = C_v + R$**   where R is the gas constant.

The relationship between Cp and Cv for nonideal gases is complex.

Example 6.2

Assuming ideal gas behavior, calculate the heat that must be transferred in each of the following cases:

1. A stream of nitrogen flowing at a rate of 100 mol/min is heated from 200°C to 100°C.
2. Nitrogen contained in a 5-liter flask at an initial pressure of 3 bar is cooled from 900°C to 30°C.

To be solved in class.