KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY CHEMICAL ENGINEERING DEPARTMENT CHE 252: CHEMICAL PROCESS CALCULATIONS II

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LECTURE 4: TABLES OF THERMODYNAMIC DATA

Learning Objectives

At the end of the lecture the student is expected to be able to do the following:

- State why the actual values of \widehat{U} and \widehat{H} can never be known for a given species in a specified state (temperature, pressure, and phase)
- Explain why the reference state used to generate a table of specific internal energies or enthalpies is irrelevant if one is only interested in calculating ΔU and ΔH for a process.
- Given a process in which a specified mass m of a species goes from one state to another and tabulated values of \hat{U} and \hat{H} for the species at the initial and final states are available, calculate ΔU and ΔH . Given values of \hat{V} at each state, calculate ΔH from the previously calculated ΔU or vice versa. Carry out the corresponding calculations to determine $\Delta \dot{U}$ and $\Delta \dot{H}$ for a stream with mass flow rate m going from one state to another.
- Explain the significance of the specific internal energies and enthalpies tabulated in the steam tables. Given any process in which a specified mass (or mass flow rate) of water changes from one state to another, use the steam tables to calculate ΔU and/or ΔH

4.1 Reference States and State Properties

It is not possible to know the absolute value of \widehat{U} and \widehat{H} for a process material, but you can determine the *change* in $\widehat{U}(\Delta\widehat{U})$ or $\widehat{H}(\Delta\widehat{H})$ corresponding to a specified change of state (temperature, pressure, and phase). This may be done, for example, by bringing a known mass m of a substance through the specified change of state in such a way that all terms of the energy balance except ΔU (i.e., heat, work, and changes in potential and kinetic energies) are known. Once $\Delta\widehat{U}(=\Delta U/m)$ has been determined, $\Delta\widehat{H}$ for the same change in state can be calculated as $\Delta\widehat{U}+\Delta P\widehat{V}$.

A convenient way to tabulate measured changes in \widehat{U} and \widehat{H} is to choose a temperature, pressure, and state of aggregation as a **reference state**, and to list $\Delta \widehat{U}$ or $\Delta \widehat{H}$ for changes from this state to a series of other states. Suppose, for example, that the enthalpy changes for carbon monoxide going from a reference state of 0°C and 1 atm to two other states are measured, with the following results:

CO(g, 0°C, 1 atm)
$$\rightarrow$$
 CO(g, 100°C, 1 atm): $\Delta \hat{H}_1 = 2919 \text{ J/mol}$
CO(g, 0°C, 1 atm) \rightarrow CO(g, 500°C, 1 atm): $\Delta \hat{H}_2 = 15,060 \text{ J/mol}$

Since \widehat{H} cannot be known absolutely, for convenience we may assign a value $\widehat{H}_o=0$ to the reference state; then $\Delta \widehat{H}_1=\widehat{H}_1-0=\widehat{H}_1$, $\Delta \widehat{H}_2=\widehat{H}_2$, and so on. A table may then be constructed for CO at 1 atm:

T(°C)	$\widehat{H}(J/mol)$	
0	0	
100	2919	
500	15,060	

Note that the value 2919 J/mol for \widehat{H} at 100°C does *not* mean that the absolute value of the specific enthalpy of CO at 100°C and 1 atm is 2919 J/mol-we cannot know the absolute value of \widehat{H} -but rather means that the *change* in \widehat{H} when CO goes from the reference state to 100°C and 1 atm is 2919 J/mol. We then say the specific enthalpy of CO at 100°C and 1 atm relative to CO at 0°C and 1 atm is 2919 J/mol.

Some enthalpy tables give the reference states on which the listed values of \widehat{H} are based and others do not; however, you do not have to know the reference state to calculate $\Delta \widehat{H}$ for the transition from one tabulated state to another. If \widehat{H}_1 is the specific enthalpy at state 1 and \widehat{H}_2 is that at state 2, then $\Delta \widehat{H}$ or the transition from state 1 to state 2 equals $\widehat{H}_2 - \widehat{H}_1$, regardless of the reference state on which \widehat{H}_1 and \widehat{H}_2 , are based. (Caution: If two different tables are used, be sure \widehat{H}_1 and \widehat{H}_2 are based on the same reference state.) For example, $\Delta \widehat{H}$ for CO going from 100 to 500°C at 1 atm is (15,060 - 2919) J/mol = 12,141 J/mol. If another reference state had been used to generate the specific enthalpies of CO at 100°C and 500°C, \widehat{H}_1 and \widehat{H}_2 would have different values but $\widehat{H}_2 - \widehat{H}_1$ would still be 12,141 J/mol. (See diagram below.)

$$\hat{H}_{CO}(J/mol)$$
 Ref: CO(g) @ 0°C, 1 atm $\hat{H}_{CO}(J/mol)$ Ref: CO(g) @ ?

 $\downarrow \downarrow$ 15,060 500°C, 1 atm 12,560 $CO(100^{\circ}C, 1 \text{ atm}) \rightarrow CO(500^{\circ}C, 1 \text{ atm})$
 $\Delta \hat{H} = (15,060 - 2919) \text{ J/mol}$
 $= (12,560 - 419) \text{ J/mol}$
 $= 12,141 \text{ J/mol}$
 $= 12,141 \text{ J/mol}$

Example 4.1*Use of Tabulated Enthalpy Data*

The following entries are taken from a data table for saturated methyl chloride:

State	T(°F)	P(psia)	$\hat{V}(ft^3/lb_m)$	$\hat{H}(Btu/lb_m)$
Liquid	-40	6.878	0.01553	0.000
Vapor	0	18.90	4.969	196.23
Vapor	50	51.99	1.920	202.28

- 1. What reference state was used to generate the given enthalpies?
- 2. Calculate $\Delta \hat{H}$ and $\Delta \hat{U}$ or the transition of saturated methyl chloride vapor from 50°F to 0°F.

SOLUTION

1. Liquid at -40° F and 6.878 psia (the state at which $\hat{H} = 0$). You do not need this information to solve part 2.

2.
$$\Delta \hat{H} = \hat{H}(0^{\circ}\text{F}) - \hat{H}(50^{\circ}\text{F}) = (196.23 - 202.28) = -6.05 \text{ Btu/lb}_{m}$$

$$\Delta \hat{U} = \Delta \hat{H} - \Delta P \hat{V} = \Delta \hat{H} - (P_{\text{final}} \hat{V}_{\text{final}} - P_{\text{initial}} \hat{V}_{\text{initial}})$$

$$= -6.05 \text{ Btu/lb}_{m}$$

$$- \frac{[(18.90)(4.969) - (51.99)(1.920)] \text{ ft}^{3} \cdot \text{psia/lb}_{m}}{1.987 \text{ Btu}}$$

$$= -4.96 \text{ Btu/lb}_{m}$$

The value of the conversion factor Btu/(ft³/psia) was obtained from the table of gas constants.

4.2 Steam Tables

The **steam tables** are a tabulation of the thermodynamic parameters for water in liquid and vapor phases. Information is provided for **saturated liquid**, **saturated steam** (i.e. saturated water vapor), and for **superheated steam** (i.e. superheated water vapor). Saturated liquid and saturated steam can coexist in a vapor liquid equilibrium. Superheated steam would have to be cooled to its dew point to become saturated. The steam tables provide the following parameters:

- i. vapor pressure of saturated water as a function of temperature (equivalently, the boiling point of liquid water as a function of pressure)
- ii. the specific volume \hat{V} of liquid water and of steam
- iii. the specific internal energies of liquid water and of steam relative to a reference state of liquid water at the triple point
- iv. the specific enthalpy of liquid water and of steam relative to a reference state of liquid water at the triple point
- v. the heat of vaporization of water, given by the difference between the enthalpies of the saturated steam and of the saturated liquid

There are three steam tables in appendices B.5 through B.7 of Elementary Principles of Chemical Processes (3rd Edition) by Richard M. Felder and Ronald W. Rousseau (2005).

Tables B.5 and B.6 provide data for saturated steam and saturated liquid. These tables apply to vapor-liquid coexistence. All of the above intensive properties are presented for both the liquid and the vapor phases. Appendix B.7 gives, in addition, the properties for superheated steam. For any of the tables you may need to use linear interpolation between the tabulated conditions to estimate the property of interest.

Example 4.2 Energy Balance on a Steam Turbine

Steam at 10 bar absolute with 190°C of superheat is fed to a turbine at a rate m=2000 kg/h. The turbine operation is adiabatic, and the effluent is saturated steam at 1 bar. Calculate the work output of the turbine in kilowatts, neglecting kinetic and potential energy changes.

Solution

The energy balance for this steady-state open system is

$$\dot{W}_{\rm s} = -\Delta \dot{H} = -\dot{m}(\hat{H}_{\rm out} - \hat{H}_{\rm in})$$

Inlet Steam

Table B.7 indicates that steam at 10 bar is saturated at 180° C so that the inlet steam temperature is 180° C + 190° C = 370° C. Interpolating in the same table.

$$\hat{H}_{in}$$
 (10 bar, 370°C) = 3201 kJ/kg

Outlet Steam

From either Table B.6 or B.7, you can find that the enthalpy of saturated steam at 1 bar is \hat{H}_{out} (1 bar, saturated) = 2675 kJ/kg

Energy Balance

$$\dot{W}_{s} = -\Delta \dot{H} = -\frac{2000 \text{ kg}}{\text{h}} \frac{(2675 - 3201) \text{ kJ}}{\text{kg}} \frac{1 \text{ h}}{3600 \text{ s}}$$

$$= 292 \text{ kJ/s} = \boxed{292 \text{ kW}}$$

The turbine thus delivers 292 kW of work to its surroundings.