KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY
CHEMICAL ENGINEERING DEPARTMENT
CHE 252: CHEMICAL PROCESS CALCULATIONS II
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LECTURE 2: ENERGY BALANCES ON CLOSED SYSTEMS

Learning Objectives

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

- Write the first law of thermodynamics (the energy balance equation) for a closed process system
- State the conditions under which each of the five terms in the balance can be neglected.
- Given a description of a closed process system, simplify the energy balance and solve it for whichever term is not specified in the process description.

A system is termed open or closed according to whether or not mass crosses the system boundary during the period of time covered by the energy balance. A batch process system is, by definition, closed, and semibatch and continuous systems are open.

An integral energy balance may be derived for a closed system between two instants of time. Since energy can neither be created nor destroyed, the generation and consumption terms of the general balance equation drop out, leaving

$$\text{accumulation} = \text{input} - \text{output} \qquad (2.1)$$

In deriving the integral mass balance for a closed system the input and output terms were eliminated, since by definition no mass crosses the boundaries of a closed system. It is possible, however, for energy to be transferred across the boundaries as heat or work, so that the right side of Equation 2.1 may not be eliminated automatically. As with mass balances, however, the accumulation term equals the final value of the balanced quantity (in this case, the system energy) minus the initial value of this quantity. Equation 2.1 may therefore be written as

$$Final\ system\ energy - Initial\ system\ energy = net\ energy\ transferred\ to\ system\ (in - out) \qquad (2.2)$$

Now

initial system energy = $U_i + E_{ki} + E_{pi}$

final system energy = $U_f + E_{kf} + E_{pf}$

energy transferred = $Q - W$

where the subscripts *i* and *f* refer to the initial and final states of the system and U, E_k, E_p, Q, and W represent internal energy, kinetic energy, potential energy, heat transferred to the system from its surroundings, and work done by the system on its surroundings. Equation 2.2 then becomes

$$(U_f - U_i) + (E_{kf} - E_{ki}) + (E_{pf} - E_{pi}) = Q - W \qquad (2.3)$$

or, if the symbol Δ is used to signify (final - initial),

$$\Delta U + \Delta E_k + \Delta E_p = Q - W \qquad (2.4)$$

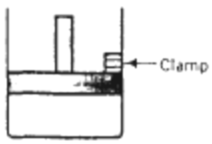
Equation 2.4 is the basic form of the first law of thermodynamics for a closed system.

When applying this equation to a given process, you should be aware of the following points:

1. The internal energy of a system depends almost entirely on the chemical composition, state of aggregation (solid, liquid, or gas), and temperature of the system materials. It is independent of pressure for ideal gases and nearly independent of pressure for liquids and solids. ***If no temperature changes, phase changes, or chemical reactions occur in a closed system and if pressure changes are less than a few atmospheres, then*** $\Delta U = 0$
2. If a system is not accelerating, then $\Delta E_k = 0$.
3. If a system is not rising or falling, then $\Delta E_p = 0$.
4. If a system and its surroundings are at the same temperature or the system is perfectly insulated, *then* $Q = 0$. The process is then termed adiabatic.
5. Work done on or by a closed system is accomplished by movement of the system boundary against a resisting force or the passage of an electrical current or radiation across the system boundary. Examples of the first type of work are motion of a piston or rotation of a shaft that projects through the system boundary. ***If there are no moving parts or electrical currents or radiation at the system boundary, then*** $W = 0$.

Example 2.1

A gas is contained in a cylinder fitted with a movable piston.



The initial gas temperature is 25°C.

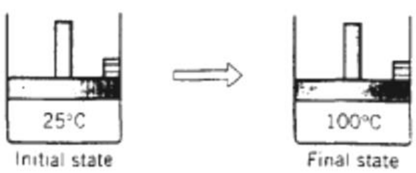
The cylinder is placed in boiling water with the piston held in a fixed position. Heat in the amount of 2.00 kcal is transferred to the gas, which equilibrates at 100°C (and a higher pressure). The piston is then released, and the gas does 100 J of work in moving the piston to its new equilibrium position.

The final gas temperature is 100°C.

Write the energy balance equation for each of the two stages of this process and in each case solve for the unknown energy term in the equation. In solving this problem, consider the gas in the cylinder to be the system, neglect the change in potential energy of the gas as the piston moves vertically, and assume the gas behaves ideally. Express all energies in joules.

Solution

1.



$$\Delta U + \Delta E_k + \Delta E_p = Q - W$$

$$\Big\Downarrow \begin{array}{rll} \Delta E_k & = 0 & \text{(the system is stationary)} \\ \Delta E_p & = 0 & \text{(no vertical displacement)} \\ W & = 0 & \text{(no moving boundaries)} \end{array}$$

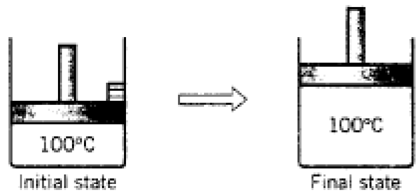
$$\Delta U = Q$$

$$\Big\Downarrow\; Q = 2.00 \text{ kcal}$$

$$\Delta U = \frac{2.00 \text{ kcal}}{} \left| \frac{10^3 \text{ cal}}{\text{kcal}} \right| \frac{1 \text{ J}}{0.23901 \text{ cal}} = \boxed{8370 \text{ J} = \Delta U}$$

The gas thus gains 8370 J of internal energy in going from 25 to 100°C.

2.



$\Delta U + \Delta E_k + \Delta E_p = Q - W$

$\Delta E_k = 0$ (the system is stationary at the initial and final states)
$\Delta E_p = 0$ (assumed negligible by hypothesis)
$\Delta U = 0$ (U depends only on T for an ideal gas, and T does not change)

$0 = Q - W$

$W = +100$ J (Why is it positive?)

$\boxed{Q = 100\text{ J}}$

Thus an additional 100 J of heat is transferred to the gas as it expands and re-equilibrates at 100°C.

Example 2.2

Alkaloids are chemical compounds containing nitrogen that can be produced by plant cells. In an experiment, a closed vessel 1.673 m^3 in volume was filled with a dilute water solution containing two alkaloids, ajmalicine, and serpentine. The temperature of the solution was 10°C. To obtain an essentially dry residue of alkaloids, all of the water in the vessel (1 kg) was vaporized. Assume that the properties of water can be used as a substitute for the properties of the solution. How much heat has to be transferred to the vessel if 1 kg of saturated liquid water initially at 10°C is completely vaporized to the final conditions of 100°C and 1 atm? See Figure E22.1.

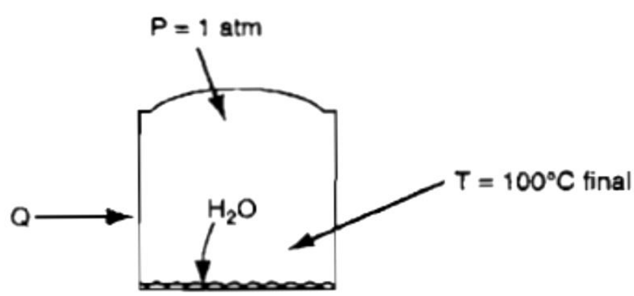


Figure E22.1

Solution

Sufficient data is given in the problem statement to fix the initial state and the final state of the water. You can look up the properties of water in the steam tables or on the CD in the back of this book. Note that the specific volume of steam at 100°C and 1 atm is 1.673 m^3/kg.

	Initial state (liquid)	Final state (gas)
p	1 atm	1 atm
T	10.0°C	100°C
$\hat{U}$	35 kJ/kg	2506.0 kJ/kg

You can look up additional properties of water such as $\hat{V}$ and $\hat{H}$, but they are not needed for the problem.

The system is closed, unsteady state so that Equation (22.2) applies

$$\Delta E = \Delta U + \Delta PE + \Delta KE = Q + W$$

Because the system (the water) is at rest, $\Delta KE = 0$. Because the center of mass of the water changes so very slightly, $\Delta PE = 0$. No work is involved (fixed tank boundary). You can conclude using a basis of

Basis: 1 kg H_2O evaporated

that

$$Q = \Delta U = m\Delta\hat{U} = m(\hat{U}_2 - \hat{U}_1)$$

$$Q = \frac{1 \text{ kg } H_2O}{} \left| \frac{(2506.0 - 35) \text{ kJ}}{\text{kg}} \right. = 2471 \text{ kJ}$$

Note: the sign conversion for work done by a system on the surroundings is + in example 1 and negative in example 2.