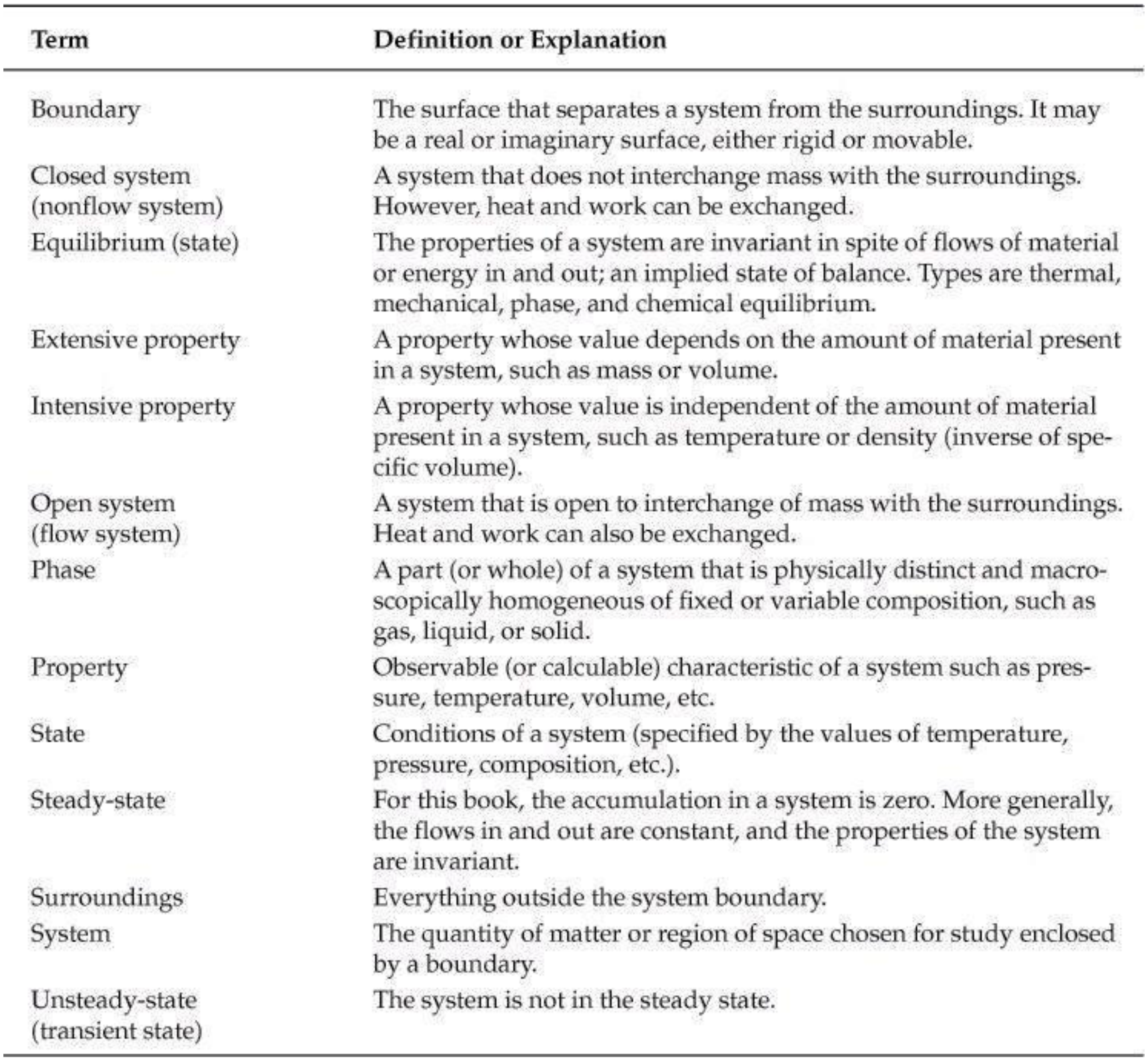
Energy Balances without Reaction

Energy itself is often defined as the capacity to do work or transfer heat, a fuzzy concept.

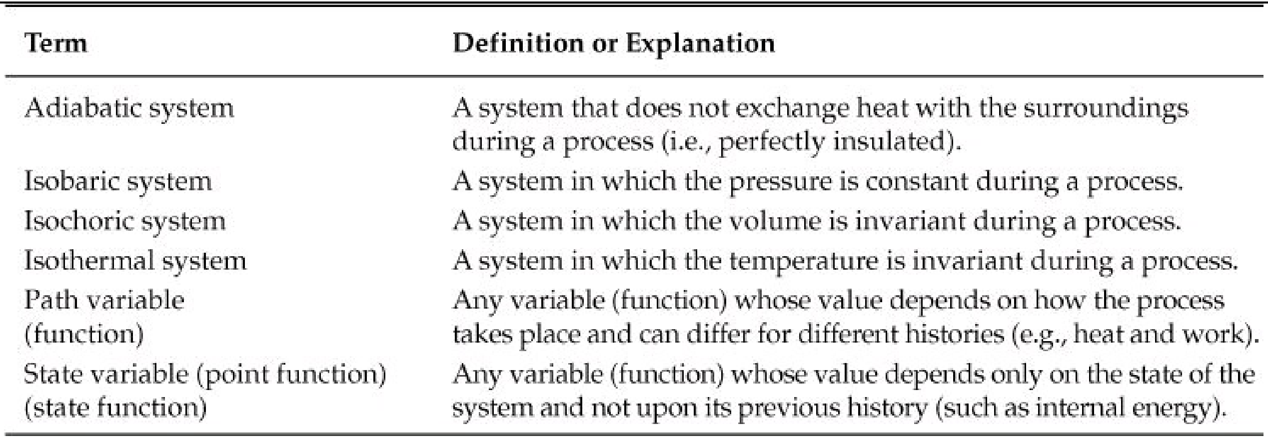
1. Terminology Associated with Energy Balances

In this lecture we will take up the second prominent topic in the petroleum and gas refining engineering principles, i.e. energy balance. So far, you have studied the details of setting up and solving material balances. An equally important and useful concept is that for energy balance. You will need both tools to solve problems in practice.

Before starting with the energy balance topic, we will first review many terms discussed in the previous chapters, namely:



Term	Definition or Explanation
Boundary	The surface that separates a system from the surroundings. It may be a real or imaginary surface, either rigid or movable.
Closed system (nonflow system)	A system that does not interchange mass with the surroundings. However, heat and work can be exchanged.
Equilibrium (state)	The properties of a system are invariant in spite of flows of material or energy in and out; an implied state of balance. Types are thermal, mechanical, phase, and chemical equilibrium.
Extensive property	A property whose value depends on the amount of material present in a system, such as mass or volume.
Intensive property	A property whose value is independent of the amount of material present in a system, such as temperature or density (inverse of specific volume).
Open system (flow system)	A system that is open to interchange of mass with the surroundings. Heat and work can also be exchanged.
Phase	A part (or whole) of a system that is physically distinct and macroscopically homogeneous of fixed or variable composition, such as gas, liquid, or solid.
Property	Observable (or calculable) characteristic of a system such as pressure, temperature, volume, etc.
State	Conditions of a system (specified by the values of temperature, pressure, composition, etc.).
Steady-state	For this book, the accumulation in a system is zero. More generally, the flows in and out are constant, and the properties of the system are invariant.
Surroundings	Everything outside the system boundary.
System	The quantity of matter or region of space chosen for study enclosed by a boundary.
Unsteady-state (transient state)	The system is not in the steady state.



Term	Definition or Explanation
Adiabatic system	A system that does not exchange heat with the surroundings during a process (i.e., perfectly insulated).
Isobaric system	A system in which the pressure is constant during a process.
Isochoric system	A system in which the volume is invariant during a process.
Isothermal system	A system in which the temperature is invariant during a process.
Path variable (function)	Any variable (function) whose value depends on how the process takes place and can differ for different histories (e.g., heat and work).
State variable (point function) (state function)	Any variable (function) whose value depends only on the state of the system and not upon its previous history (such as internal energy).

Adiabatic means no heat transfer occurs between the system and its surroundings across the system boundary. Under what circumstances might a process be adiabatic?

- The system is insulated.
- ***Q*** is very small in relation to the other terms in the energy equation and maybe neglected.
- The process takes place so fast that there is no time for heat to be transferred.

2. Types of Energy to Be Included in Energy Balances

2.1 Heat (Q)

As a single term, is the net amount of heat transferred to or from the system over a fixed time interval. ***Heat (Q)*** is commonly defined as that part of the total energy flow across a system boundary that is caused by a temperature difference (potential) between the system and the surroundings (or between two systems). “heat” when meaning “heat transfer” or “heat flow.” Because heat is based on the transfer of energy, heat cannot be stored. Heat is positive when transferred to the system and negative when removed from the system. Heat is a path variable. Keep in mind that a process in which no heat transfer occurs is an adiabatic process ($Q = 0$).

Heat transfer is usually classified in three categories: conduction, convection, and radiation. To evaluate heat transfer quantitatively, you can apply various empirical formulas to estimate the heat transfer rate. One example of such a formula is the rate of heat transfer by convection that can be calculated from:

$$\dot{Q} = U^{*}A(T_2 - T_1)$$

Q is the rate of heat transfer (such as joules per second).

A is the area for heat transfer (such as square meters).

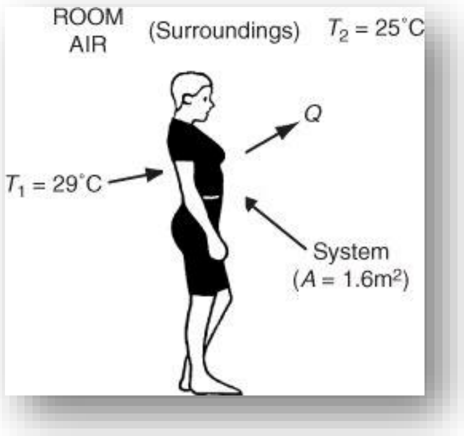
(**T_2 – T_1**) is the temperature difference between the surroundings at T_2 and the system at T_1 (such as in degrees Celsius).

U* is an empirical coefficient usually determined from experimental data for the equipment involved; it might have the units of $J/(s)(m^2)(°C)$.

Example 1: Convection

Ignoring conduction and radiation, the convective heat transfer from a person (the system) to a room (the surroundings) can be calculated using U* = 7 $W/(m^2)(°C)$ and the data in Figure below.

Solution $Q=\frac{7\ W}{m^2\ {}^oC}\times 1.6\ m^2\times(25-29)^oC=-44.8\ W\ \ or\ -44.8\ {}^J\!/_s$



Note that is negative because heat is transferred from the system to the surroundings. Multiply by the period in hours to get Q in watt-hours. What is the value of the rate of heat transferred into the air if the air is the system? It is +44.8 W.

2.2 Work (W)

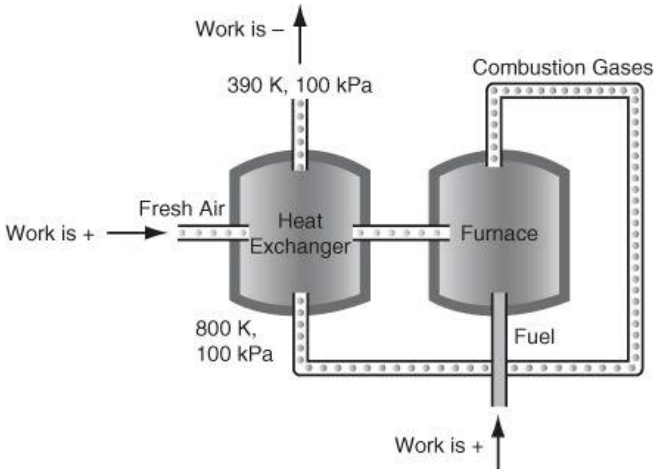
Work is a form of energy that represents a transfer of energy between the system and surroundings. Work cannot be stored. Work is a *path variable*. Work is positive when the surroundings perform work on the system. Work is negative when the system performs work on the surroundings.

Many types of work can take place (which we will lump together under the notation W), among which `are the following:

Mechanical work: Work that occurs because of a mechanical force that moves the boundary of a system.

Electrical work: Electrical work occurs when an electrical current passes through an electrical resistance in the circuit. If the system generates an electrical current (e.g., an electrical generator inside the system) and the current passes through an electrical resistance outside the system, the electrical work is negative because the electrical work is done on the surroundings. If the electrical work is done inside the system because of an applied voltage from outside the system, the electrical work is positive. **Shaft work:** occurs when the system causes a shaft to turn against an external mechanical resistance. When a source of water outside the system circulates in the system and consequently causes a shaft to turn, the shaft work is positive.

Flow work: Flow work is performed on the system when fluid is pushed into the system by the surroundings. Look at the Figure below. For example, when a fluid enters a pipe, some work is done on the system (the water that already is in the pipe) to force the new fluid into the pipe. Similarly, when fluid exits the pipe, the system does some work on the surroundings to push the exiting fluid into the surroundings.



To calculate the mechanical work:

a. For constant pressure (isobaric process): $W = \int_{V_1}^{V_2} p\,dV = p\left(V_2 - V_1\right)$

b. For constant temperature (isothermal process):

$$W = \int_{V_1}^{V_2} p\,dV = p\left(V_2 - V_1\right) = \frac{nRT}{V}dV$$

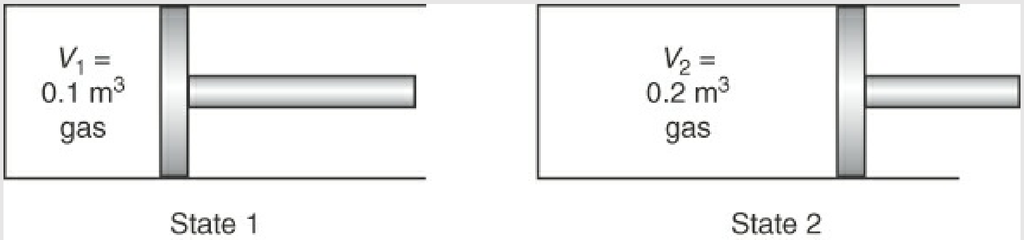
$$W = nRT\ln\frac{V_2}{V_1}$$

Example 2: Calculation of Mechanical Work by a Gas on a Piston

Suppose that an ideal gas at 300 K and 200 kPa is enclosed in a cylinder by a *frictionless (ideal) piston* and the gas slowly forces the piston so that the volume of gas expands from 0.1 to 0.2 m3. Examine the Figure below. Calculate the work done by the gas on the piston (the only part of the system boundary that moves) if two different paths are used to go from the initial state to the final state.

Path *A*: The expansion occurs at constant pressure (**isobaric**) (*p* = 200 kPa).

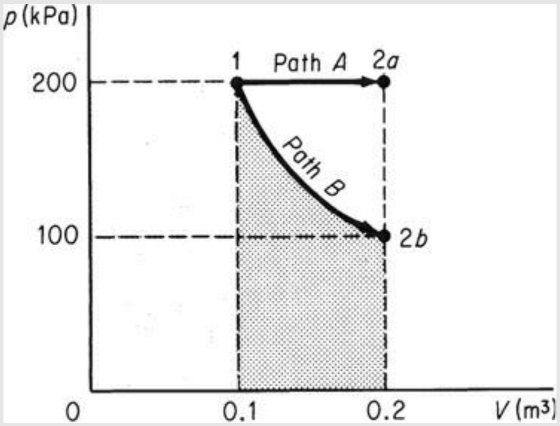
Path *B*: The expansion occurs at constant temperature (**isothermal**) (*T* = 300 K)



Solution

$$n = \frac{200\ \text{kPa}}{} \bigg| \frac{0.1\ \text{m}^3}{} \bigg| \frac{}{300\ \text{K}} \bigg| \frac{(\text{kg mol})(\text{K})}{8.314(\text{kPa})(\text{m}^3)} = 0.00802\ \text{kg mol}$$

Note that by definition, the work done by the system is *negative*. If the integral *dV* is positive (such as in expansion), the value of the integral will be positive and *W* negative (work done on the surroundings). If *dV* is negative, *W* will be positive (work done on the system).



Path *A* (the constant pressure process):

$$W = -p\int_{V_1}^{V_2} dV = -p(V_2 - V_1)$$

$$= -\frac{200\times 10^3\ \text{Pa}}{}\left|\frac{1\ \text{N}}{1(\text{m}^2)(\text{Pa})}\right|\frac{0.1\text{m}^3}{}\left|\frac{1\ \text{J}}{1(\text{N})(\text{m})}\right. = -20\ \text{kJ}$$

Path B (the constant temperature process):

$$W = -\int_{V_1}^{V_2} \frac{n\text{RT}}{V} dV = -n\text{RT}\ln\left(\frac{V_2}{V_1}\right)$$

$$= -\frac{0.00802\ \text{kg mol}}{}\left|\frac{8.314\ \text{kJ}}{(\text{kg mol})(\text{K})}\right|\frac{300\,\text{K}}{}\ln 2 = -13.86\ \text{kJ}$$

2.3 Internal Energy

Internal energy is the energy contained within the system excluding the kinetic energy of motion and the potential energy. It is a macroscopic concept that takes into account all of the molecular, atomic and subatomic energies. Because no instruments exist with which internal energy can be measured, internal energy must be calculated from other certain variables that can be measured macroscopically such as pressure, volume, temperature and composition.

, $\hat{U}$ can be differential with respect to T and $\hat{V}$. By taking the total derivative, we find that:

$$d\hat{U} = \left(\frac{\partial \hat{U}}{\partial T}\right)_{\hat{V}} dT + \left(\frac{\partial \hat{U}}{\partial \hat{V}}\right)_{T} d\hat{V}$$

By definition $\left(\frac{\partial \hat{U}}{\partial T}\right)_{\hat{V}}$ is the **heat capacity** (specific heat) at constant volume, given the special symbol C_v. ***Cv*** can also be defined to be the amount of heat necessary to raise the the temperature of 1 kg of a substance by 1 degree in a closed system and so has the SI units of J/(kg)(K), if the process is carried out at constant volume. Consequently, *changes in the internal energy* over a specified time interval can usually be computed by integrating the above as follows:

$$\Delta\hat{U} = \hat{U}_2 - \hat{U}_1 = \int_{\hat{U}_1}^{\hat{U}_2} d\hat{U} = \int_{T_2}^{T_1} C_v\, dT$$

Note that you can only calculate differences in internal energy or calculate the internal energy relative to a *reference state* but not absolute values of internal energy. For example, the reference condition can be taken at 298 K:

The initial state of system (1): $U_1 - U_{ref}$

The final state of system (2): $U_2 - U_{ref}$

The reference energy cancels out when you calculate the internal energy difference:

$$\text{Net internal energy change} = \left(U_2 - U_{ref}\right) - \left(U_1 - U_{ref}\right) = U_2 - U_1$$

Example 3: Calculation of an Internal Energy Change Using the Heat Capacity

What is the change in internal energy when 10 kg mol of air is cooled from 60°C to 30°C in a constant volume process? C_v is 2.1 × 10^4 J/(kg mol)(°C) over the temperature range.

Solution

$$\Delta U = 10\,\text{kg} \int_{60^\circ\text{C}}^{30^\circ\text{C}} \left(2.1\times10^4 \frac{\text{J}}{(\text{kg mol})(^\circ\text{C})}\right) dT$$
$$= 2.1\times10^5\,(30-60) = -6.3\times10^6\ \text{J}$$

Closed, Unsteady-State Examples

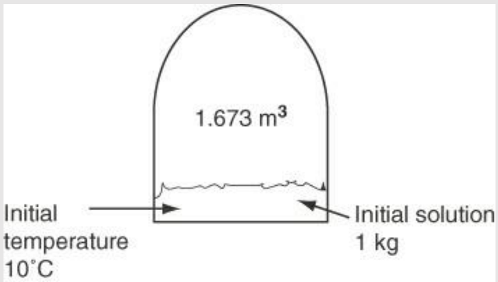
For a closed, unsteady-state system, the energy balance is given by:

$$\Delta U = Q + W$$

In closed systems, the values of ΔPE and ΔKE in ΔU_{total} are usually negligible or zero; hence, the above Equation does not include these terms.

Example 4: Application of the Energy Balance to a Closed System

An insulated closed vessel 1.673 m^3 in volume was injected with a dilute water solution containing two alkaloids. The temperature of the solution was 10°C. To obtain an essentially dry residue of alkaloids, all of the water in the vessel was vaporized. Assume that the properties of water can be used in place of the properties of the solution. How much heat had to be transferred to the vessel if 1 kg of saturated liquid water initially at 10°C was completely vaporized to a final condition of 100°C and 1 atm? See Figure below. Ignore any air present in the vessel (or assume an initial vacuum existed)



Solution

The system is a closed vessel in an unsteady state. Sufficient data are 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 steam tables. Note that the specific volume of steam at 100°C and 1 atm is 1.673 m3/kg.

Initial state (liquid)	Final state (gas)	
p	vapor pressure	1 atm
T	10.0°C	100°C
Ú	17.7 kJ/kg	2506.0 kJ/kg

$$\Delta U = Q + W$$

No work is involved (fixed tank boundary, no engine in the system). You can conclude, using

Basis: 1 kg of H_2O evaporated

that

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

$$Q = \frac{1\ \text{kg H}_2\text{O}}{} \left| \frac{(2506.0 - 17.7)\ \text{kJ}}{\text{kg}} \right. = 2488\ \text{kJ}$$

Homework: Ten pounds of water at room temperature (80°F) are stored in a sealed tank that has a volume of 4.0 ft^3. How much heat must be transferred to the tank so that 40% of the water is vaporized? Also, what will be the final temperature and pressure?

2.4 Kinetic Energy (KE)

Kinetic Energy is the energy a system, or some material, possesses because of its velocity relative to the surroundings, which are usually, but not always, at rest. The wind, moving automobiles, waterfalls, flowing fluids, and so on possess kinetic energy. The equation used to calculate the *KE* is:

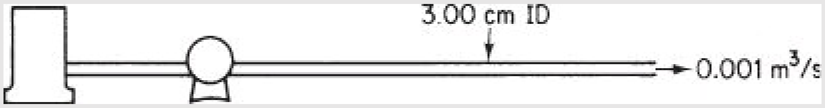
$$KE = \frac{1}{2}mv^2$$

The kinetic energy per unit mass (the specific kinetic energy), a state variable, is

$$\widehat{KE} = \frac{1}{2}v^2$$

Example 5. Calculation of the Specific Kinetic Energy for a Flowing Fluid

Water is pumped from a storage tank through a tube of 3.00 cm inner diameter at the rate of 0.001 m^3/s. See Figure below. What is the specific kinetic energy of the water in the tube?



Solution:

Basis: 0.001 m^3 equivalent to 1 s

Assume that

$$\rho = \frac{1000\ \text{kg}}{\text{m}^3} \qquad \text{and} \quad r = \frac{1}{2}(3.00) = 1.50\ \text{cm}$$

$$v = \frac{0.001\ \text{m}^3}{\text{s}}\left|\frac{}{\pi(1.50)^2\ \text{cm}^2}\right|\left(\frac{100\ \text{cm}}{1\ \text{m}}\right)^2 = 1.415\ \text{m/s}$$

$$K\hat{E} = \frac{1}{2}\left|\left(\frac{1.415\ \text{m}}{\text{s}}\right)^2\right|\frac{1\ (\text{N})(\text{s}^2)}{1(\text{kg})(\text{m})}\left|\frac{1\ \text{J}}{1(\text{N})(\text{m})}\right. = 1.00\ \text{J/kg}$$

2.4 Potential Energy (PE)

Potential energy (PE): is the energy the system possesses because of the force exerted on its mass by a gravitational field for a reference surface. You can calculate the potential energy in a gravitational field from:

$$PE = mgh$$

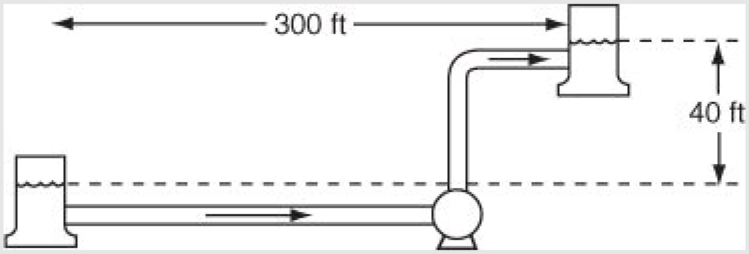
or the specific potential energy

$$\hat{PE} = gh$$

where *h* is the distance from the reference surface, and where the overlay (^) means potential energy per unit mass. The measurement of h is made to the center of mass of a system.

Example 6. Calculation of Potential Energy of Water

Water is pumped from one reservoir to another 300 ft away, as shown in the Figure below. The water level in the second reservoir is 40 ft above the water level of the first reservoir. What is the increase in specific potential energy of the water in British thermal units per pound (mass)?



Solution

$$\Delta\hat{PE} = \frac{32.2\ \text{ft}}{\text{s}^2}\left|\frac{(40-0)\ \text{ft}}{}\right|\frac{1\ (\text{lb}_\text{f})(\text{s}^2)}{32.2\ (\text{lb}_\text{m})(\text{ft})}\left|\frac{1\ \text{Btu}}{778.2\ (\text{ft})(\text{lb}_\text{f})}\right. = 0.0514\ \text{Btu}/\text{lb}_\text{m}$$

2.5 Enthalpy (H)

Enthalpy is a measurement of energy in a thermodynamic system. It is equal to the internal energy of the system plus the product of pressure and volume:

$$H = U + pV$$

We will express the enthalpy in terms of the temperature and pressure (the former is a more convenient variable than the specific volume). If we let:

$$\hat{H} = \hat{H}(T, p)$$

by taking the total derivative of H we can form an expression analogous to the Equation:

$$d\hat{H} = \left(\frac{\partial \hat{H}}{\partial T}\right)_p dT + \left(\frac{\partial \hat{H}}{\partial p}\right)_T dp$$

By definition $(\partial\hat{H}/\partial T)_p$ is the heat capacity at constant pressure and is given the special symbol C_p

$$\Delta\hat{H} = \hat{H}_2 - \hat{H}_1 = \int_{H_1}^{H_2} d\hat{H} = \int_{T_1}^{T_2} C_p dT$$

One property of ideal gases, but not of real gases, to remember is that their enthalpies and internal energies are functions of temperature only and are not influenced by changes in pressure or specific volume. Also, the relation between Cp and Cv for an ideal gas is ***Cv = Cp – R.***

NOTE that the units of all the forms of energy is **J** in SI units and **Btu** in AE units

Example 7. Calculation of an Enthalpy Change

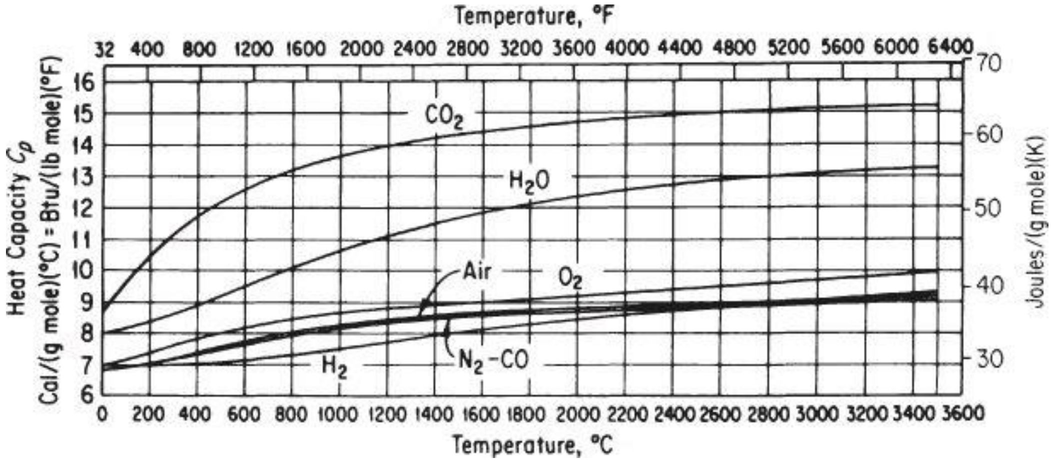
What is the change in internal energy when 10 kg mol of air is cooled from 60°C to 30°C in a constant volume process? C_p at 1 atm is a constant over the temperature range with a value of 2.913 × 104 J/(kg mol)(°C) at 45°C.

Solution

$$\Delta H = 10 \text{ kg mol} \int_{60^\circ\text{C}}^{30^\circ\text{C}} (2.9 \times 10^4) \frac{\text{J}}{(\text{kg mol})(^\circ\text{C})} dT = 2.9 \times 10^5 (30 - 60)$$
$$= -8.7 \times 10^6 \text{ J}$$

2.6 Heat Capacity

Heat capacity is defined as the change in temperature of a system with a change of heat transferred to the system.



If you can assume the gas is ideal, the heat capacity at constant pressure is constant even though the temperature varies

Type of Molecule*	Approximate Heat Capacity, C_p High Temperature (Translational, Rotational, and Vibrational Degrees of Freedom)	Room Temperature (Translational and Rotational Degrees of Freedom Only)
Monoatomic	$\frac{5}{2}R$	$\frac{5}{2}R$
Polyatomic, linear	$\left(3n - \frac{3}{2}\right)R$	$\frac{7}{2}R$
Polyatomic, nonlinear	$(3n - 2)R$	$4R$

*n, number of atoms per molecule; R, gas constant.

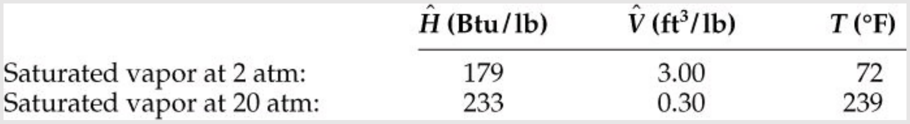
Most of the equations for the heat capacities of solids, liquids, and gases are empirical. You usually find that the heat capacity at constant pressure, C_p, is expressed as a function of temperature for a specified range of temperature. A power series in temperature, with constants a, b, c, and so on, are typically used to model the temperature dependence of C_p. For example

$$C_p = a + bT + cT^2$$

Example 8. Use of the Pressure-Enthalpy Chart for Butane to Calculate the Enthalpy Difference between the Two States

Calculate $\Delta\hat{H}$, $\Delta\hat{V}$, and ΔT for 1 lb of saturated vapor of n-butane going from 2 atm to 20 atm (saturated).

Solution:



	$\hat{H}$ (Btu/lb)	$\hat{V}$ (ft^3/lb)	T (°F)
Saturated vapor at 2 atm:	179	3.00	72
Saturated vapor at 20 atm:	233	0.30	239

$$\Delta\hat{H} = 233 - 179 = 54 \text{ Btu/lb}$$

$$\Delta\hat{V} = 0.30 - 3.00 = -2.70 \text{ ft}^3\text{/lb}$$

$$\Delta T = 239 - 72 = 167°\text{F}$$