

The First Law of Thermodynamics

Energy cannot be created or destroyed, it can only change form.

For using the First Law in calculations, you must first define your system, and in particular your system boundary.

Work, W , is done by a force acting through a distance. In differential form:

$$dW = Fdx.$$

For closed systems, work is energy crossing the system boundary due to deformation of the boundary. If there is a pressure, P , being exerted by the system on its surroundings over an area, A , and the area is displaced by a distance, dx , then we have

$$PA = F, dW = Fdx = PA dx = P(Adx) = PdV$$

or in integrated form

$$W = \int PdV.$$

Heat, Q , is energy crossing the system boundary due to a temperature difference.

Thermodynamics was developed by engineers to describe heat engines (things that convert heat to work). They desired to put heat in and get work out, so in E82 and in Felder and Rousseau, *heat into* a system is *positive*, and *work out* of a system is *positive*.

Chemists like to confuse things by having both heat and work in as positive. Ignore them.

Energy may be stored in things as position in a conservative field (potential energy, $E_p = mgz$), velocity in a reference frame

(kinetic energy, $E_k = \frac{1}{2}mv^2$) and in microscopic vibrations, oscillations and such (internal energy, U). For a **closed system** the First Law can be written in differential form as

$$dU + dE_p + dE_k = dQ - dW$$

or in integrated form as

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

Much of the work in a First Law problem is deciding which terms are zero or insignificant.

Intensive and Extensive Properties

A property of a substance that *does not* depend on the mass or moles of a substance is an *intensive* property (such as temperature, pressure, or composition).

A property of a substance that *does* depend on the mass or moles of a substance is an *extensive* property (such as volume, kinetic energy, or internal energy).

It is quite frequently useful to define an intensive property that is related to the extensive property. These intensive properties

are specific properties and are usually indicated by a circumflex, e.g., specific volume, $\hat{V} = V/n$, or specific internal energy, $\hat{U} = U/n$.

Enthalpy (pronounced en-THAL-pee)

Enthalpy, H , is a defined quantity that is quite useful in simplifying formulas. It is defined as

$$H \equiv U + PV ,$$

or in specific properties as

$$\hat{H} \equiv \hat{U} + P\hat{V} .$$

One example where enthalpy is useful is where a closed system doesn't change velocity or position and is maintained at constant pressure (like in a beaker in a laboratory). Under these conditions the First Law simplifies from

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

to

$$\Delta U = U_{final} - U_{initial} = Q - W = Q - \int P dV = Q - P \int dV$$

$$U_{final} - U_{initial} = Q - P(V_{final} - V_{initial})$$

$$(U_{final} + PV_{final}) - (U_{initial} + PV_{initial}) = Q$$

$$\Delta H = Q .$$

For an **open steady-state system**, all of the quantities are expressed as rates (with the dot). The work is normally divided up into *shaft work*, \dot{W}_s , (work done by or on a shaft crossing the system boundary, such as to a turbine), and flow work, \dot{W}_{fl} , (work done on or by the system to push the flowing fluid into or out of the system).

$$\dot{W} = \dot{W}_s + \dot{W}_{fl}$$

$$\dot{W}_{fl} = \sum_{\text{outputs}} P_i \dot{V}_i - \sum_{\text{inputs}} P_j \dot{V}_j$$

If one starts with the first law for an open system,

$$\Delta \dot{U} + \Delta \dot{E}_p + \Delta \dot{E}_k = \dot{Q} - \dot{W}$$

and divides the work into shaft work and flow work, and combines the flow work with the internal energy, one arrives at

$$\Delta \dot{H} + \Delta \dot{E}_p + \Delta \dot{E}_k = \dot{Q} - \dot{W}_s,$$

which is the first law for an open steady-state system.

Remember Δ means *final – initial* for closed systems and *out – in* for open systems. If you have multiple streams, you must sum over all of the streams.

Simplifications

These simplifications are exact, there is no approximation involved.

No change in elevation, $\Delta E_p = 0$

No change in velocity, $\Delta E_k = 0$

Adiabatic or insulated, $Q = 0$

Volume remains constant, closed system, $W = 0$.

No shafts cross boundary e.g., from a turbine, compressor, or pump), open system, $\dot{W}_s = 0$

Ideal gas, no chemical reaction, $T = \text{constant}$, $\Delta U = 0$, $\Delta H = 0$

Approximations

These approximations are usually pretty good, but recognize that they are approximations.

Evaporation, Condensation, Chemical Reaction, Large Temperature Changes, $\Delta E_k \approx 0$, $\Delta E_p \approx 0$, $W \approx 0$

Solid or liquid, no chemical reaction, $T = \text{constant}$, $\Delta P = \text{small}$, $\Delta U = 0$, $\Delta H = 0$

Mechanical Energy Balance

In an open, steady-state system with no chemical reaction or phase change, if the density of the fluid is constant, and the only heating is by friction, the First Law can be simplified to

$$\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\Delta z + \hat{F} = \frac{-\dot{W}_s}{\dot{m}}$$

For a circular pipe, \hat{F} can be calculated as

$$\hat{F} = 4f \frac{L u^2}{D},$$

where L is the length of the pipe, D is the diameter of the pipe, and u is the velocity of the fluid. f is the *Fanning Friction Factor*, and is a function of the *Reynolds Number*. The Reynolds Number is an important dimensionless quantity in fluid mechanics. For a pipe, it is calculated as

$$\text{Re} = \frac{\rho u D}{\mu} \text{ or } \text{Re} = \frac{u D}{\nu},$$

where D is the diameter of the pipe, u is the velocity of the fluid, ρ is the density of the fluid, μ is the dynamic viscosity of the fluid, and $\nu = \mu/\rho$, is the kinematic viscosity of the fluid. For $\text{Re} < 2100$, the flow in the pipe is *laminar* and $f = 16/\text{Re}$. For $\text{Re} > 2300$, the flow is *turbulent*, and f has to be evaluated from a

chart called a *Moody Chart*. To use a *Moody Chart* you have to

5-22 FLUID DYNAMICS

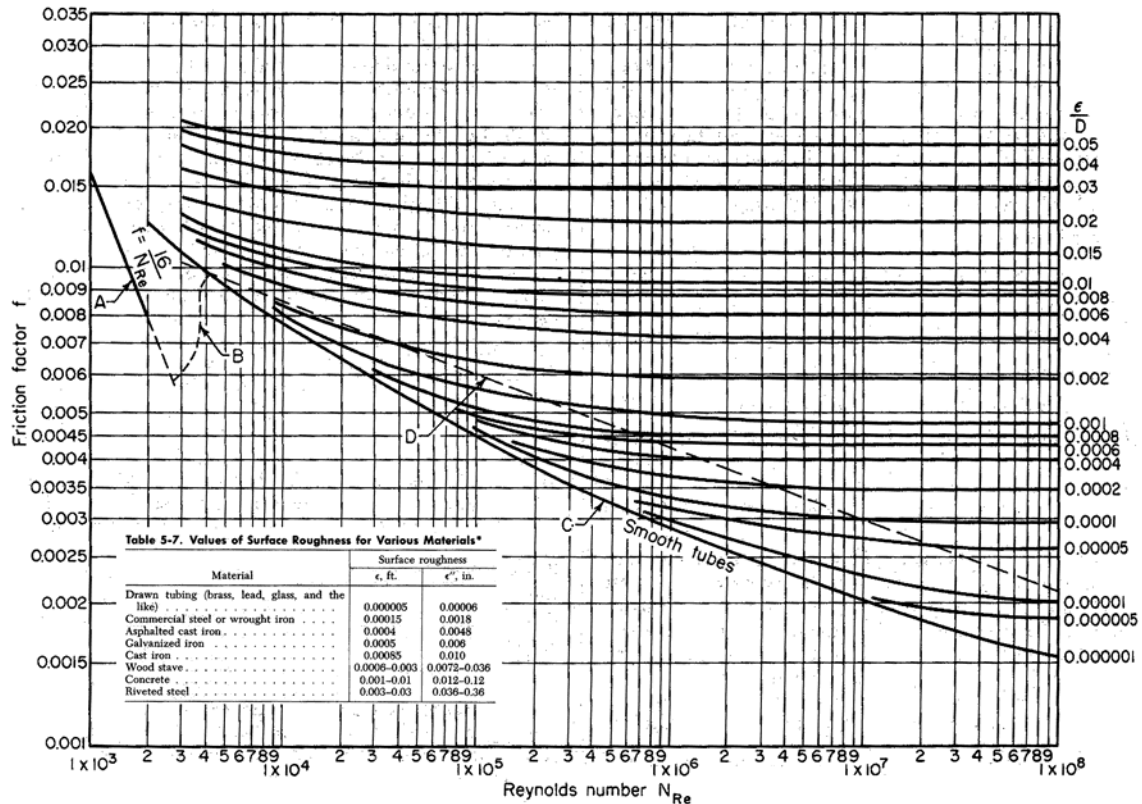


Fig. 5-26. Fanning friction factors. Reynolds number $N_{Re} = DV\rho/\mu$, where D = pipe diameter, ft.; V = velocity, ft./sec.; ρ = fluid density, lb./cu. ft.; μ = fluid viscosity, lb./(ft.)(sec.) = cp./1488. [Based on Moody, *Trans. Am. Soc. Mech. Engrs.*, 66, 671 (1944).]

know the Reynolds Number and the *Surface Roughness* of the inside of the pipe. In addition to the Fanning Friction Factor, there is another Friction Factor called the *Moody, Darcy, or Blasius Friction Factor*. It is also given the symbol f . The relationship is

$$4f_{\text{Fanning}} = f_{\text{Moody}}$$

Make sure you know which one you are using. As a rule-of-thumb, Chemical Engineers use the Fanning Friction Factor and Mechanical Engineers use the Moody Friction Factor. The website has Moody Charts for each.

Example Problem

Water at 20°C flows at 0.05 m³/s in a 20 cm asphalted cast iron pipe. Calculate ΔP per kilometer.

Properties: $\rho = 998 \text{ kg/m}^3$, $\mu = 1.00 \times 10^{-3} \text{ N s/m}^2$.

$$\text{Calculate velocity: } u = \frac{\dot{V}}{A} = \frac{0.05 \text{ m}^3/\text{s}}{\frac{\pi}{4}(0.20 \text{ m})^2} = 1.59 \text{ m/s}$$

$$\text{Re} = \frac{\rho u D}{\mu} = \frac{998 \text{ kg/m}^3 (1.59 \text{ m/s}) 0.20 \text{ m}}{(1.00 \times 10^{-3} \text{ N s/m}^2)} = 3.18 \times 10^5$$

Look up the surface roughness in the table on the Moody Chart.

$$\varepsilon = 0.0004 \text{ ft.}$$

The most common mistake is to forget to calculate ε/D from ε .

$$\frac{\varepsilon}{D} = \frac{4 \times 10^{-4} \text{ ft} (0.3048 \text{ m/ft})}{0.20 \text{ m}} \approx 0.0007$$

From the Moody Chart (for Fanning not Moody Friction factor)

$$f = 0.0048$$

$$F = 4f \frac{L}{D} \frac{u^2}{2} = 4(0.0048) \left(\frac{1000}{0.2} \right) \frac{(1.59)^2}{2} = 121 \text{ m}^2/\text{s}^2$$

Simplify the mechanical energy balance:

$$\frac{\Delta P}{\rho} + \cancel{\frac{\Delta u^2}{2}} + \cancel{g\Delta z} + \hat{F} = \cancel{\frac{-\dot{W}_s}{\dot{m}}}$$

$$\text{Then, } \Delta P = -\rho \hat{F} = \left(998 \frac{\text{kg}}{\text{m}^3}\right) \left(121 \frac{\text{m}^2}{\text{s}^2}\right) = 121 \text{ kPa} = 1.2 \text{ atm}.$$