

FIGURE 4.1 State, path, and inexact differentials. Left: Integrating with exact differential calculates zero distance. Right: Inexact differential using $\delta x = \text{sgn}(dx)dx$.

one-dimensional coordinates x (the “state”). Now in the second case use the exact differential $\int_{x_1}^{x_1} dx =$

$x_1 - x_1 = 0$. This means that there is no change of state but we know that we traveled twice as much as in the first case. We can clarify the situation by integrating separately for each path,

first in the positive x direction and second in the negative x direction: $\int_{x_1}^{x_2} dx + \int_{x_2}^{x_1} (-dx) =$

$(x_2 - x_1) + (-1)(x_1 - x_2) = 2(x_2 - x_1)$. We traveled twice as much and this makes more sense. We can generalize this process with an inexact differential defined as $\delta x = \text{sgn}(dx)dx$, where sgn is the

sign or *signum* function. The sign function is defined as $\text{sgn}(x) = \begin{cases} -1 & \text{if } x < 0 \\ 0 & \text{if } x = 0 \\ +1 & \text{if } x > 0 \end{cases}$

and it is the derivative of the absolute value of x . Then, $\int_{x_1}^{x_2} \delta x + \int_{x_2}^{x_1} \delta x = \int_{x_1}^{x_2} \text{sgn}(dx)dx + \int_{x_2}^{x_1} \text{sgn}(dx)dx =$

$\int_{x_1}^{x_2} dx + \int_{x_2}^{x_1} -dx = 2(x_2 - x_1)$. In essence, we have used an *integration factor* to convert an inexact differential to an exact one.

Example 4.1

Suppose you move in a straight line from point $x_1 = 10$ m to point $x_2 = 20$ m and then return half-way between these two points. What is the change of state? What is the distance traveled? The answer is straightforward; the change of state is 5 m and the distance is 15 m, but use inexact differentials and the sgn function for practice. Answer: The change of state is

$$\int_{x_1}^{(x_2+x_1)/2} dx = ((x_2 + x_1)/2 - x_1) = (x_2 - x_1)/2 = (20 - 10)/2 = 5 \text{ m}$$

The distance is found by integration with inexact differential using the ~~sign~~ ^{sgn} function

$$\int_{x_1}^{x_2} \delta x + \int_{x_2}^{(x_2+x_1)/2} \delta x = \int_{x_1}^{x_2} \text{sgn}(dx)dx + \int_{x_2}^{(x_2+x_1)/2} \text{sgn}(dx)dx$$

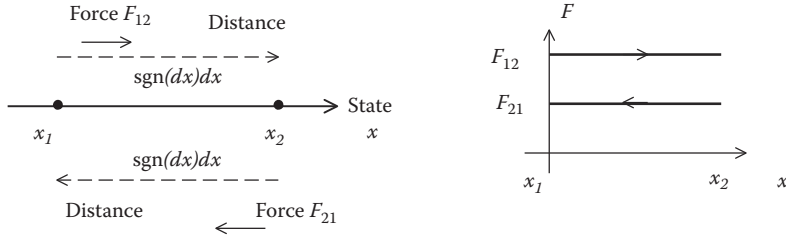


FIGURE 4.2 Work and inexact differentials. Force has different value in positive x direction compared to negative x direction.

same temperature; however, the heat exchanged was not zero. If we integrate with exact differential, we would get an incorrect result of zero energy transfer. Using an inexact differential resolves the

issue. Therefore we could write $Q = \int_1^2 \delta Q$ as in Equation 4.1. For a gas, we can transfer heat at

constant volume and therefore the pressure will vary, or we can transfer heat at constant pressure and thus the volume will change. Specific heat capacity differs whether the process is at constant volume or constant pressure, therefore the heat transfer depends on the path.

4.1.3 STATEMENT OF THE FIRST LAW: CONSERVATION OF ENERGY

The first law of thermodynamics is the principle of *conservation of energy*: In order to “produce” energy in one form we need to spend energy in another form. In other words, energy can only be transformed, not created. Said another way, we cannot devise a machine or process that continuously produces energy without any corresponding input. A formal statement of the first law requires considering the *internal energy*, U , of a *closed system* and its relationship to possible external inflow and outflow of energy. Thermodynamically, a closed system is one that *does not exchange matter* with its surroundings; it only exchanges heat Q and work W (Figure 4.3).

Internal energy is a state function. When the system is closed and there is no exchange of energy in the form of work or heat, its internal energy is constant and therefore its change is zero:

$$dU = 0 \quad (4.2)$$

As the system exchanges heat and work with its surroundings, there is a change in internal energy:

$$dU = \delta W + \delta Q \quad (4.3)$$

This is the *first law of thermodynamics*. Note that work and heat are given with inexact differentials to acknowledge the fact that they are path functions, as explained in the previous section. However, internal energy is a state function and given by an exact differential.

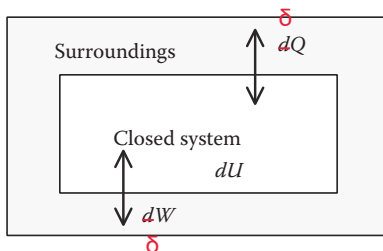


FIGURE 4.3 Conceptualization of a closed system.

Example 4.9

Consider one mole of air at 1 bar and 25°C (nearly SATP). Recall from Example 4.4 that it should occupy 24.78 liters. Assume we pressurize it to 2 bar keeping the volume constant. What are the specific work, heat, and internal energy changes? Answer: For an isochoric process $W = 0$, and to

calculate heat use $Q = \int_1^2 c_v(T) n dT$. To simplify, $c_v(T)$ is assumed constant and equal to its value at

middle of the temperature range, which is from 25°C to $T_2 = \frac{P_2 V_1}{nR} = \frac{200 \text{ k} \times 24.78 \times 10^{-3}}{1 \times 8.314} = 596.1 \text{ K}$ or 323.1°C. The middle of the range is approximately $(323 + 25)/2 \approx 174^\circ\text{C}$ and at that temperature c_v the specific heat can be found quickly from

```
> cp.cv(TC=(323+25)/2)$cv
[1] 21.365
>
```

Note that we have used \$cv to get the molar cv component directly. Then use 21.365 kJ/(molK) to calculate $Q = c_v n \Delta T = 21.365 \times (323.1 - 25) \approx 6.37 \text{ kJ}$. This result can be expressed as specific heat divided by mass $q = Q/(nM) = 6.37/(1 \times 28.97/10^3) \approx 219.8 \text{ kJ/kg}$. The specific internal energy is $\Delta u = q - w \approx 219.8 \text{ kJ/kg}$.

Here we have calculated total heat using molar heat capacity and then divided by mass to obtain specific heat and specific internal energy. Alternatively, we can first calculate mass, use specific heat capacity on a per kg basis, and calculate specific heat, work, and internal energy directly. The following example illustrates this alternative method.

Example 4.10

Consider one mole of air at 1 bar and 25°C (nearly SATP). Recall from Example 4.4 that it should occupy 24.78 liters. We let it expand to 34.78 l keeping pressure constant at 1 bar. What are the specific work, heat, and internal energy changes? Answer: The mass in kg is $m = nM = 1 \text{ mol} \times 28.97 \text{ g/mol} \times 10^{-3} \text{ kg/g} \approx 0.02897 \text{ kg}$. For this isobaric path, specific work is

$w = -P\Delta V / m = -100 \text{ k} \times 0.01/0.02897 = -34.52 \text{ kJ/kg}$. The final temperature is $T_2 = \frac{P_1 V_2}{nR} = \frac{100 \text{ k} \times 34.78 \times 10^{-3}}{1 \times 8.314} = 418.33 \text{ K}$ or $\sim 145.33^\circ\text{C}$. The c_p value for the middle of the range is found from

```
> cp.cv(TC=(145+25)/2)$cp.kg
[1] 1.012
>
```

using $c_p = 1.012 \text{ kJ/(kgK)}$ constant, $q = c_p \Delta T = 1.012 \times (145.33 - 25) = 121.74 \text{ kJ/kg}$. The specific internal energy change is $\Delta u = q - w = (121.77 - 34.52) \text{ kJ/kg} = 87.25 \text{ kJ/kg}$.

These calculations are time consuming and not exact if there is wide variation in T since we assumed the heat capacities to be constant. We can expedite calculations using function

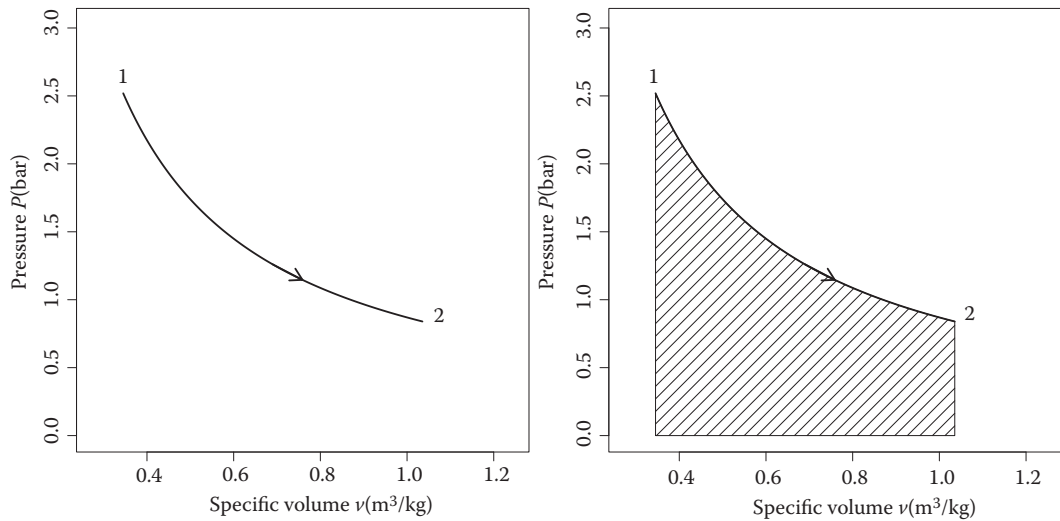


FIGURE 4.6 P - v graph of isotherm^{a1} expansion. Work is the integral of P or the shaded area under the curve. Left: 1–2: isotherm, expansion $30^\circ\text{C} \rightarrow 30^\circ\text{C}$, $W = -95.5 \text{ kJ/kg}$, $Q = 95.5 \text{ kJ/kg}$. Right: 1–2: isotherm, expansion $30^\circ\text{C} \rightarrow 30^\circ\text{C}$, $W = -95.5 \text{ kJ/kg}$, $Q = 95.5 \text{ kJ/kg}$.

$nRT \ln \left(\frac{V_2}{V_1} \right)$. Here nRT is taken out of the integral because the path is isothermal. You must realize that to keep T constant while the gas expands we must add heat to avoid cooling. The first law then predicts that the heat added must equal the work done to avoid a change in U , that is to say, $\Delta U = 0 = Q - W$ and therefore $Q = W$. The isotherm just obtained assumes the path is reversible; it is done gradually to keep the gas in equilibrium with the surroundings at all times. In other words, the gas pressure is the same as the external pressure P_{ext} while traversing the path.

If the process were to be irreversible, the work is reduced. For example, expanding the gas freely against the external pressure $P_2 = P_{ext}$, the work is $W = P_{ext} \int_1^2 dV = P_2(V_2 - V_1) = nRT \frac{V_2 - V_1}{V_2}$. This work is less than the one for a reversible process since $\ln \left(\frac{V_2}{V_1} \right) > \frac{V_2 - V_1}{V_2}$. We will further interpret this difference when we discuss entropy in Chapter 6.

Using Equation 4.11 we can express work indistinctly using the ratio of pressures or the ratio of volumes

$$W = nRT \ln \left(\frac{V_2}{V_1} \right) = nRT \ln \left(\frac{P_1}{P_2} \right) \quad (4.12)$$

This work is the area under an isotherm curve like the one shown in Figure 4.6 (right-hand side), which is obtained using `argument shade.under=TRUE` in the list of `x`:

```
x<-list(V=c(10,30),T=c(30,NA),path='isotherm',lab=c("1","2"),shade.under=TRUE)
path.lines(x)
```

Example 4.12

Consider reversible isothermal expansion of Example 4.10, where one mole of air previously compressed three times with respect to final volume and held at 30°C. What is the specific work done? Answer: We use Equation 4.12 $W = nRT \ln \left(\frac{V_2}{V_1} \right) = 1 \times 8.314 \times 303 \times \ln \left(\frac{3}{1} \right) \text{ J} = 2.767 \text{ kJ}$. Then divide by mass 0.02897 kg to get $w = -95.51 \text{ kJ/kg}$. Note that this value of work is printed inside the legend box in Figure 4.6. It is equal and opposite sign to the heat because we assume it to be a reversible process.

Figure 4.7 shows two isotherm paths at different temperatures and the corresponding work as shaded areas. Work is larger for the higher-temperature isotherm (left-hand side) and includes the work done by the lower-temperature one. The difference of work between the two corresponds to the shaded area in between (right-hand side). This figure is obtained using **PV.lines** as follows:

```
x1 <- list(V=c(10,30),T=c(200,200),path='isotherm',lab=c("3","4"))
x2 <- list(V=c(10,30),T=c(30,30),path='isotherm',lab=c("1","2"))
x <- list(x1,x2)
path.lines(x,shade.between=TRUE)
```

4.2.7 ADIABATIC PATHS

Consider PV work to be done by a closed system with an expanding gas $\delta W = -PdV$ but without adding heat $\delta Q = 0$. This is an *adiabatic* process; the first law reduces to $dU = \delta W + \delta Q = -PdV$.

Equate this to Equation 4.7 so that we can write $ndT = -\frac{PdV}{c_v}$. Now use the gas law $ndT = -\frac{nRT}{V} \frac{dV}{c_v}$

and rearrange to get ready for integration of each side $\frac{dT}{T} = -\frac{R}{c_v} \frac{dV}{V}$. If we assume c_v to be constant,

we can integrate between state 1 and 2 $\ln \left(\frac{T_2}{T_1} \right) = -\frac{R}{c_v} \ln \left(\frac{V_2}{V_1} \right)$ or $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\frac{R}{c_v}}$. Now because

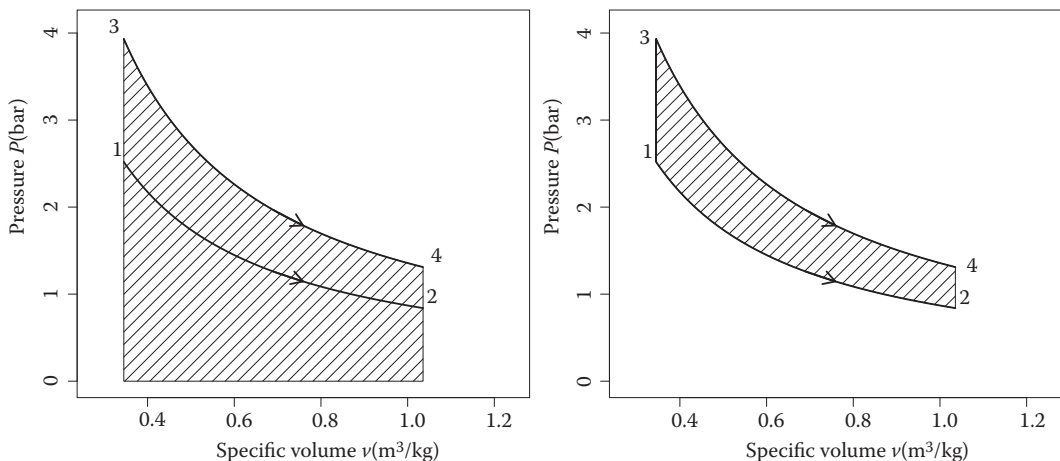


FIGURE 4.7 Two isotherms. Difference in work done by each expansion is the shaded area between the curves. Left: 1–2: isotherm, expansion 30°C → 30°C, $W = -95.5 \text{ kJ/kg}$, $Q = 95.5 \text{ kJ/kg}$; 3–4: isotherm 200°C → 200°C, $W = -149.1 \text{ kJ/kg}$, $Q = 149.1 \text{ kJ/kg}$. Right: 1–2: isotherm expansion 30°C → 30°C, $W = -95.5 \text{ kJ/kg}$, $Q = 95.5 \text{ kJ/kg}$; 3–4: isotherm, expansion 200°C → 200°C, $W = -149.1 \text{ kJ/kg}$, $Q = 149.1 \text{ kJ/kg}$.

The system goes from state 1 to 2 in an adiabatic reversible path, thus the heat transferred is zero; the only contribution to internal energy is work done on the gas δW to compress it. Using the first

law, Equation 4.3, $U_2 - U_1 = \int_1^2 \delta W = W_{12}$. The temperature increases from that one of the LTR $T_L = \frac{P_1 V_1}{nR}$ to the HTR $T_H = \frac{P_2 V_2}{nR}$.

Then, from state 2 to 3 the gas performs work while it expands at constant temperature T_H (isothermal reversible expansion at the HTR) requiring heat input Q_H . Since $dT = 0$, there is zero change in internal energy $\Delta U = U_3 - U_2 = 0 = Q_H - W_{23}$; therefore, $Q_H = \int_2^3 \delta W$. The integral is

$W_{23} = \int_2^3 P dV$ and it is the area under the curve of the upper trace of the cycle. Using Equation 4.12, $Q_H = W_{23} = nRT_H \ln \left(\frac{V_3}{V_2} \right)$.

From state 3 to 4, the gas expands along a reversible adiabatic path, which means that $U_4 - U_3 =$

$-\int_3^4 W = -W_{34}$, dropping from the HTR to the LTR. Finally, the working fluid will return to state 1 by reversible isothermal (at T_C) compression, losing heat Q_C , thus the change in internal energy is zero $U_1 - U_4 = 0 = Q_L - W_{41}$. During this part of the cycle, work is done on the fluid. The integral $W_{41} = \int_4^1 P dV$ is the area under the curve of the lower trace $Q_L = W_{41} = nRT_L \ln \left(\frac{V_1}{V_4} \right)$.

Combining the changes of internal energy for all the paths of the cycle, we have $(U_2 - U_1) + (U_3 - U_2) + (U_4 - U_3) + (U_1 - U_4) = U_1 - U_1 = 0$ because we have returned to a state with the same energy. However, this does not mean that heat or work are zero because they are path functions integrated along the cycle.

Integration of a path function along a cyclical path is represented by $X = \oint \delta x$. Succinctly, we can write $\oint \delta Q = \oint \delta W$ to say that in a cycle, net exchanges of work and heat are equal so that the internal energy does not change. Consider heat and integrate along individual paths that make up the cycle

$Q = \oint \delta Q = \int_1^2 \delta Q + \int_2^3 \delta Q - \int_3^4 \delta Q - \int_4^1 \delta Q = 0 + Q_H - 0 - Q_L$ or simply $Q = Q_H - Q_L$. Similarly for

work, $W = \oint \delta W = \int_1^2 \delta W + \int_2^3 \delta W - \int_3^4 \delta W - \int_4^1 \delta W = W_{12} - W_{23} - W_{34} + W_{41}$, which is

the area of the polygon enclosed by the cycle (Figure 4.12). We conclude that $Q_H - Q_L = W$, which is the heat engine equation.

The net difference in heat is

$$Q_H - Q_L = nRT_H \ln \left(\frac{V_3}{V_2} \right) - nRT_L \ln \left(\frac{V_1}{V_4} \right) \quad (4.17)$$