Lecture 11

Internal Energy and Enthalpy for Fluids

Last Time

Reversible, Quasistatic, and Quasiequilbrium Processes

Maximizing Work is Minimizing Power

Models for Gases

Internal Energy of an Ideal Gas

We will show that the internal energy of an ideal gas is a function of temperature only. This makes physical sense because there is an assumption in ideal gas behavior that there is no interaction between the molecules when we write $P\overline{V} = RT$

Start with a reversible process for an ideal gas:

$$dU = dq + dw = dq - PdV \tag{11-1}$$

Consider two processes: one occurring at constant volume, the other occurring at constant pressure.

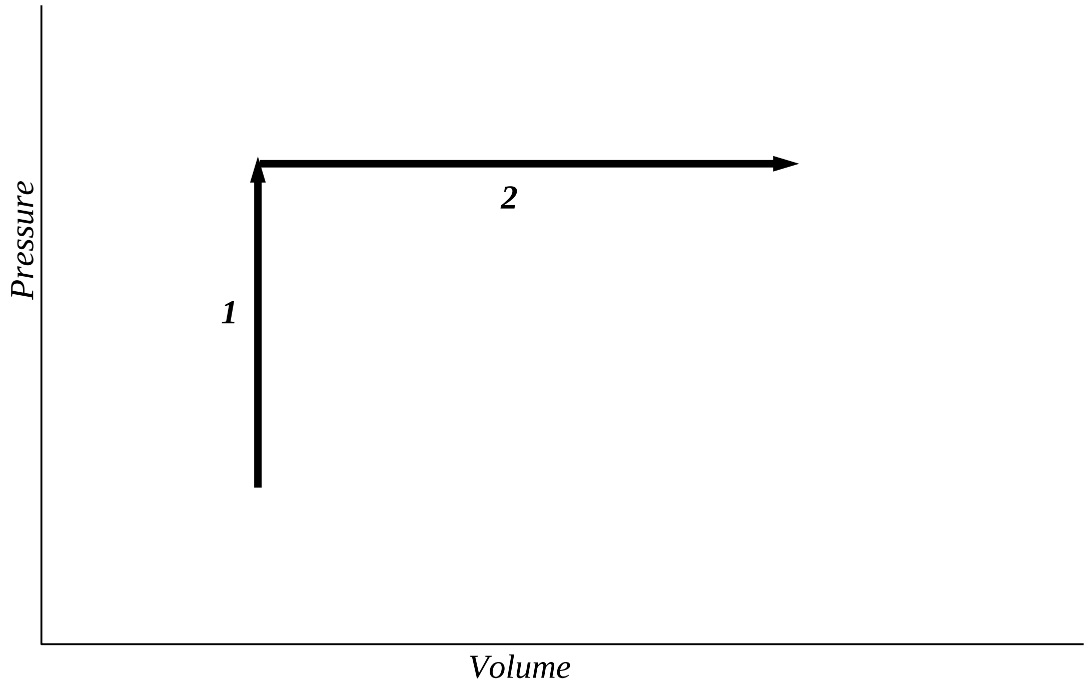

Figure 11-1: Two consecutive processes, constant volume followed by constant pressure.

For process 1: $dU = C_V dT + 0$; This can be integrated because T is the only thing that is changing on the righthandside (C_V is assumed to be independent of T and V).

For process 2: $dU = C_P dT - PdV$; P is constant (i.e., not a function of T or V) so it can be integrated directly. Using the ideal gas law:

$$\begin{aligned} PV &= nRT \\ PdV + VdP &= nRdT \\ PdV = nRdT & \quad \text{(constant pressure)} \end{aligned} \tag{11-2}$$

So for process 2,

$$dU = (C_P - nR)dT \tag{11-3}$$

Because we can make up any quasi-static curve with segments of dV processes and dP processes

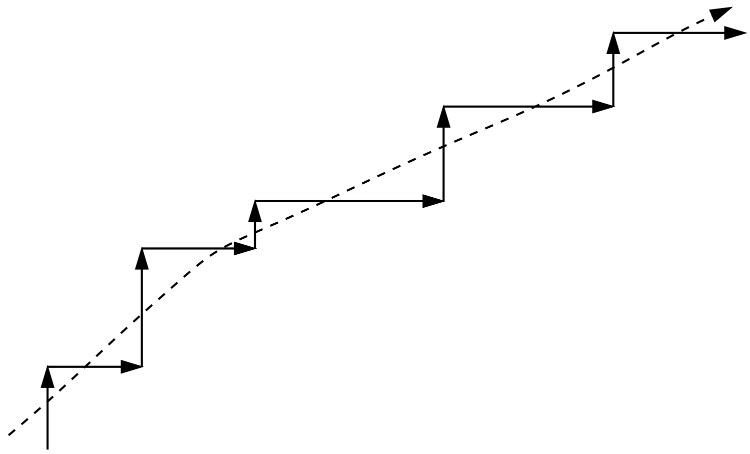

Figure 11-2: Any curve can be made up of short segments in the limit.

Evidently, the sum of any such processes is a function only of T. Therefore, for an ideal gas

$$U(T, n) \quad \text{or} \quad \overline{U}(T) \tag{11-4}$$

Comparing the two equations:

$$dU = C_V dT \tag{11-5}$$

for the constant volume process, and

$$dU = (C_P - nR)dT \tag{11-6}$$

for the constant pressure process:

$$\int_{\text{initial}}^{\text{final}} dU = \int_{T_i}^{T_f} C_V dT \quad \text{and} \quad \int_{\text{initial}}^{\text{final}} dU = \int_{T_i}^{T_f} (C_P - nR)dT \tag{11-7}$$

$$\Delta U = U_{\text{final}} - U_{\text{initial}} = C_V(T_{\text{final}} - T_{\text{initial}}) \tag{11-8}$$

$$\Delta U = (C_P - nR)(T_{\text{final}} - T_{\text{initial}}) \tag{11-9}$$

$$C_P - C_V = nR \tag{11-10}$$

or

$$\overline{C_P} - \overline{C_V} = R \tag{11-11}$$

A New Thermodynamic State Function: Enthalpy

For an simple pure fluid, consider the physical meaning of the $-PV$ term alone;

Question: What are the units of PV? What are the units of P?

Imagine that there is a completely homogeneous system that has been arbitrarily divided into small volumes of size dV:

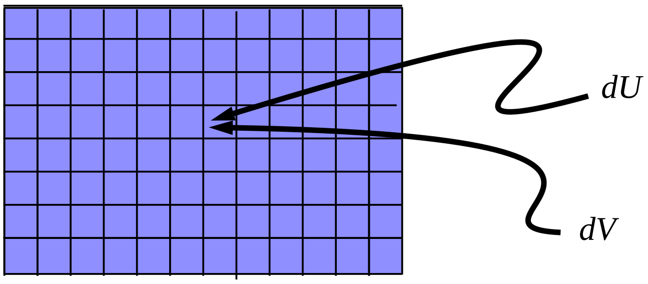

Figure 11-3: A uniformly homogeneous system (i.e. uniform pressure) of a simple pure fluid divided into an arbitrary of smaller systems of size dV

Consider what is left of the internal energy after we subtract off the "mechanical" or "compression" energy:

$$\begin{array}{ccc} \text{Total Internal Energy} & - & \text{Total Mechanical Energy} \\ \int_{\text{system}} dU & - & \int_{\text{system}} (-P) dV \\ U & + & PV \end{array} \tag{11-12}$$

The reason that the integration can be carried out is that both dV and dU are extensive variables and are thus additive for each subsystem.

So that we can define a new state function (that is also extensive),

$$H = U + PV \tag{11-13}$$

It is sensible to interpret H as the "thermal energy" at constant pressure. In other words, we divide the internal energy for a simple fluid U into two parts—one part corresponding to that stored as compressive energy $(-PV)$ and another part the thermal energy H. Another way to see this is:

$$\begin{aligned} dH &= dU + PdV + VdP \\ &= dq - PdV + PdV + VdP \\ &= dq + VdP \end{aligned} \tag{11-14}$$

In other words

$$\left(\frac{\partial H}{\partial T}\right)_{P=\text{constant}} = \left.\frac{dq}{dT}\right|_{P=\text{constant}} \equiv C_P \tag{11-15}$$

for an ideal gas:

$$H - U = PV = nRT \quad \text{or} \quad \frac{d(\overline{H} - \overline{U})}{dT} = R = \overline{C_P} - \overline{C_V} \tag{11-16}$$

Another State Function

Recall that dq is not a perfect differential.
Let's consider dq for an ideal gas undergoing a reversible process.

$$dq_{rev} = dU + PdV \tag{11-17}$$

for an ideal gas

$$dq_{rev} = C_V dT + PdV \tag{11-18}$$

$$dq_{rev} = C_V dT + \frac{nRT}{V} dV \tag{11-19}$$

Now divide through by T

$$\frac{dq_{rev}}{T} = \frac{C_V}{T} dT + \frac{nR}{V} dV \tag{11-20}$$

Notice that we have separated the equation into something that is integrable over segments of dT and dV and thus over any curve.

Therefore, dq_{rev}/T is a "perfect differential" and it must then be a state function for an ideal gas.