

Lapse Rate. Prof. Ruiz (Doc), UNC-Asheville (1978-2021), [DoctorPhys on YouTube](#).

Prerequisites: Chemistry, Physics I, II. Calculus I, II, III. Thermodynamics.

**Chapter F. Enthalpy.** We have seen the first law of thermodynamics discussed in the previous chapter as

$$dU = \delta Q - \delta W,$$

where we can include  $\delta W = pdV$  for a gas.

The first law is then

$$dU = \delta Q - pdV.$$

We divide by the  $m$  of the gas and introduce some notational definitions.

$$dU = \delta Q - pdV \Rightarrow \frac{dU}{m} = \frac{\delta Q}{m} - p \frac{dV}{m} \Rightarrow du = \delta q - pd\alpha$$

This equation is labeled (13) from the last chapter.

Solve for  $\delta q$ .

$$\delta q = du + pd\alpha$$

Remember that we employ the delta symbol  $\delta$  with  $q$  to remind us that heat  $q$  is not a variable of the gas state. Heat can enter or leave the gas, but it is the energy of the gas that is a valid variable to describe the actual state of the gas when things settle down. We say that the gas is in equilibrium. But note that the variables  $u$ ,  $p$ , and  $\alpha$  are all acceptable variables that can be assigned to the gas. We can make differentials of these with no problem:  $du$ ,  $dp$ , and  $d\alpha$ . We call these standard differentials exact differentials, while  $\delta q$  is referred to as an inexact differential.

We would like to have variable of the gas state that is closely aligned with heat. Since  $\delta q = du + pd\alpha$  we note that the right side  $du + pd\alpha$  suggests that we consider  $du + pd\alpha + \alpha dp$ .

The combination  $du + pd\alpha + \alpha dp$  can be expressed as  $du + d(\alpha p)$ , which we can readily recognize as an exact differential  $d(u + \alpha p)$ . We define  $u + \alpha p$  as the *enthalpy*  $h$ .

$$h = u + \alpha p$$

Enthalpy is a variable of the gas state as it is defined as a combination of the state variables  $u$ ,  $\alpha$ , and  $p$ . All state variables can be expressed in differential form, i.e., exact differentials.

The definition of the enthalpy state variable brings us to our next review equation.

$$(13) \boxed{h = u + p\alpha}$$

Note that there is a well-defined enthalpy for each equilibrium state of a gas. Remember that equilibrium means constant temperature and pressure throughout the gas. No matter what path you take in a thermodynamic process to go from an initial point  $i$  to a final point  $f$ , the change in enthalpy is the difference of enthalpies:  $\Delta h = h_f - h_i$ . It is path independent. This difference behaves as any state variable difference such as the change in specific pressure  $\Delta p = p_f - p_i$  or specific volume

$$\Delta \alpha = \alpha_f - \alpha_i$$

Now consider our first law of thermodynamics  $du = \delta q - p d\alpha$  and  $dh = d(u + p\alpha)$ .

$$du = \delta q - p d\alpha \quad \Rightarrow \quad \delta q = du + p d\alpha$$

$$dh = d(u + p\alpha) \quad \Rightarrow \quad dh = du + p d\alpha + \alpha dp \quad \Rightarrow \quad du = dh - p d\alpha - \alpha dp$$

We substitute  $du = dh - p d\alpha - \alpha dp$  in  $\delta q = du + p d\alpha$  next.

$$\delta q = du + p d\alpha \quad \Rightarrow \quad \delta q = dh - \cancel{p d\alpha} - \alpha dp + \cancel{p d\alpha} \quad \Rightarrow \quad \delta q = dh - \alpha dp$$

We arrive at our 14<sup>th</sup> equation.

$$(14) \boxed{\delta q = dh - \alpha dp}$$

While we cannot talk about heat  $q$  content in a gas since it is not a state variable, we can talk about enthalpy of the gas, which is closely related to heat. In fact, for cases of no change in pressure,  $\delta q = dh - \alpha dp = dh - \alpha \cdot 0 = dh$ , and  $\delta q$  becomes an exact differential!