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## LECTURE 17: MAXWELL RELATIONS

Friday, February 21, 2020

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From last lecture, we decided we don't really care about the number of particles, and we can write partial derivatives in terms of Jacobians:

$$\left. \frac{\partial P}{\partial T} \right|_{V,N} \equiv \left. \frac{\partial P}{\partial T} \right|_V = \frac{\partial(P,V)}{\partial(T,V)} = \frac{\partial(P,V)}{\partial(P,T)} \frac{\partial(P,T)}{\partial(T,V)}$$

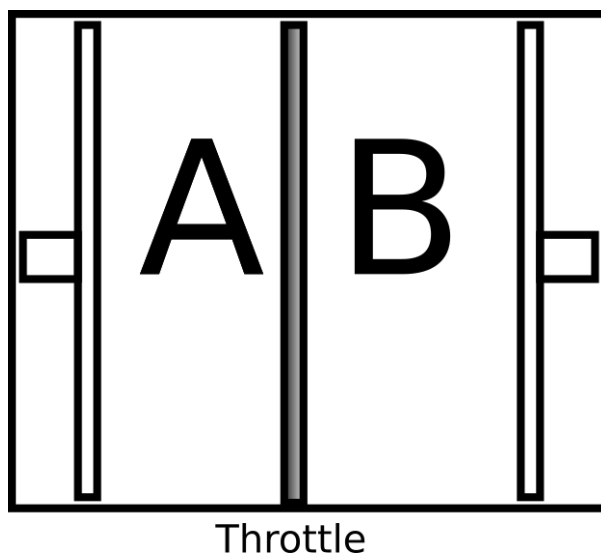
Typically, we want to introduce a Jacobian made of the variables used in the original derivative (in this case,  $P$  and  $T$ ). It usually makes for a simple transformation, but it is obviously not the only possibility. For the magic to work out, we need things to be in the same "slot", and switching ordering means introducing minus signs:

$$-\frac{\partial(V,P)}{\partial(T,P)} \frac{\partial(P,T)}{\partial(V,T)} = -\left. \frac{\partial V}{\partial T} \right|_P \left. \frac{\partial P}{\partial V} \right|_T$$

We can then use inverses:

$$-\left. \frac{\partial V}{\partial T} \right|_P \left. \frac{\partial P}{\partial V} \right|_T = \frac{\frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P}{-\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T} = \frac{\alpha}{K_T}$$

### 0.1 The Joule-Thomson Effect



**Figure 0.1.1:** Demonstration of the Joule-Thomson Effect

Fun fact, Thomson is William Thomson, aka Kelvin. Let's imagine a container with two pistons (see Figure 0.1.1). The gas in compartment  $A$  is at pressure  $P_A$  and the gas in  $B$  is at  $P_B$ . Suppose we start with  $P_A > P_B$  and we maintain this while moving the pistons such that the gas moves from compartment  $A$  to compartment  $B$ . The energy in  $B$  can be written

$$U_B = U_A + P_A V_A - P_B V_B$$

Note that this implies the enthalpy stays constant (isenthalpic process):

$$H_A = U_A + P_A V_A = U_B + P_B V_B = H_B$$

How does the temperature of the gas change? For a small pressure difference at constant  $N$  and  $H$ , we have

$$dT = \left. \frac{\partial T}{\partial P} \right|_{H,N} dP = \mu_{JT}$$

where  $\mu_{JT}$  is the “Joule-Thomson coefficient”. If  $\mu_{JT} > 0$ , the gas cools in the process. Let’s use Maxwell relations to transform this into something we can measure:

$$\mu_{JT} = \left. \frac{\partial T}{\partial P} \right|_{H,N} = \frac{\partial(T, H)}{\partial P, H} = -\frac{\partial(T, H)}{\partial(T, P)} \frac{\partial(T, P)}{\partial(H, P)} = -\frac{\left. \frac{\partial H}{\partial P} \right|_T}{\left. \frac{\partial H}{\partial T} \right|_P}$$

Next, let’s work out what these derivatives are. Recall the enthalpy  $H(S, P, N)$  has a differential form:

$$dH = T dS + V dP + \mu dN$$

We agreed at doing this at constant  $N$ , so we really only need  $dH = T dS + V dP$ .

$$\left. \frac{\partial H}{\partial P} \right|_T = T \left. \frac{\partial S}{\partial P} \right|_T + V \left. \frac{\partial P}{\partial T} \right|_T$$

We can justify this with the chain rule:

$$\begin{aligned} \left. \frac{\partial H(S, P, N)}{\partial P} \right|_{T,N} &= \left. \frac{\partial H}{\partial S} \right|_{P,N} \left. \frac{\partial S}{\partial P} \right|_{T,N} + \left. \frac{\partial H}{\partial P} \right|_{S,N} \left. \frac{\partial P}{\partial P} \right|_{T,N} + \left. \frac{\partial H}{\partial N} \right|_{S,P} \left. \frac{\partial N}{\partial P} \right|_{T,N} \\ &= T \left. \frac{\partial S}{\partial P} \right|_{T,N} + V \left. \frac{\partial P}{\partial P} \right|_{T,N} + \mu \left. \frac{\partial N}{\partial P} \right|_{T,N} \end{aligned}$$

$$\frac{\partial P}{\partial P} = 1$$

so we really only need to find

$$\left. \frac{\partial S}{\partial P} \right|_T = - \left. \frac{\partial V}{\partial T} \right|_P$$

using Maxwell’s relations.

How does the volume change while keeping the pressure fixed? This is typically thought of as the thermal expansion, but we need that  $\frac{1}{V}$  factor to make it into the defined material property:

$$\left. \frac{\partial H}{\partial P} \right|_T = -TV \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P + V = V(1 - T\alpha)$$

Now for the denominator:

$$\left. \frac{\partial H}{\partial T} \right|_P = T \left. \frac{\partial S}{\partial T} \right|_P + V \left. \frac{\partial P}{\partial T} \right|_P + (dN \text{ stuff}) = N \frac{T}{N} \left. \frac{\partial S}{\partial T} \right|_P = NC_p$$

Therefore,

$$\mu_{JT} = -\frac{V(1 - T\alpha)}{NC_p} = -\frac{V}{NC_p}(T\alpha - 1)$$

What happens when we do this with an ideal gas?

$$\alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P = \frac{1}{V} \frac{\partial}{\partial T} \left( \frac{Nk_B T}{P} \right) = \frac{1}{V} \frac{Nk_B}{P} = \frac{1}{T}$$

Therefore,  $\mu_{JT, \text{ideal}} = 0$ ! We can’t use ideal gasses to enact the Joule-Thomson effect to cool or heat a gas.