J02T.1

Problem:

A thermally isolated vessel containing a non-ideal gas is separated in two parts by a porous barrier. Initially all of the gas is on one side of the barrier and occupies a volume V. The gas is transferred slowly through the barrier by moving two pistons inward and outward, while keeping the pressures P_1 and P_2 fixed on both sides of the barrier. This is called a Joule-Thomson process. For an ideal gas the temperatures T_1 and T_2 before and after the process are the same. For a non-ideal gas there wil be a small difference $\Delta T = T_2 - T_1$. The problem is to determine ΔT for a non-ideal gas described by the van der Waals equation of state:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{1}$$

In this problem, we assume that the pressure difference is small, so that after the process the volume has increased only by a small amount $\Delta V = V_2 - V_1$.

Soltuion:

1.Calculate the free energy $F(V,T)$ for a van der Waals gas with total specific heat C_V .

Given the relation between the pressure and volume, we find that:

$$\left(\frac{\partial F}{\partial V}\right)_T = -P = \frac{a}{V^2} - \frac{RT}{V-b} \tag{2}$$

Thus, integrating once, we get:

$$F = -\frac{a}{V} - RT\ln(V-b) + c(T) \tag{3}$$

where $c(T)$ is some arbitrary function of temperature.

Next, we determine $c(T)$ from the specific heat C_V .

$$C_V = \frac{\partial U}{\partial T} = -\frac{\partial}{\partial T}\left(T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right) \tag{4}$$

After simplifying, we get:

$$c''(T) = \frac{-C_V}{T} \tag{5}$$

so that:

$$c(T) = -C_V T \ln T + cT \tag{6}$$

where c is just a integration constant.

Putting everything together, we find:

$$F(T,V) = -\frac{a}{V} - RT\ln(V-b) - C_V T \ln T + cT \tag{7}$$

2. Show that the enthalpy $H \equiv U + PV$ is constant for a Joule-Thomson process.

Note that

$$dH = dU_1 + dU_2 + dP_1 \cdot V_1 + dP_2 \cdot V_2 + P_1 \cdot dV_1 + P_2 \cdot dV_2 \tag{8}$$

But we are keeping the pressure constant, ie, $dP = 0$. Writing out, $dU = dQ - P \cdot dV$ and $dQ_1 + dQ_2 = 0$, it's easy to see that H is constant.

3. Find the enthalpy H for a van der Waals gas as a function of V and T

Again, simply plugging in P:

$$H = U + PV = C_V T + V\left(\frac{RT}{V-b} - \frac{a}{V^2}\right) \tag{9}$$

4.Show that ΔT is positive for high temperature and negative for low temperatures. The temperature T_{inv} at which ΔT changes sign is called the inversion temperature. Derive T_{inv}

The inversion temperature changes sign when:

$$\left(\frac{\partial T}{\partial V}\right) = -\left(\frac{\left(\frac{\partial H}{\partial V}\right)}{\left(\frac{\partial H}{\partial T}\right)}\right) = 0 \tag{10}$$

Explicitly:

$$\left(\frac{\partial T}{\partial V}\right) = -\frac{\frac{2a}{V^2} + RT(\frac{-b}{(V-b)^2})}{C_V + \frac{RV}{V-b}} \tag{11}$$

Solve this equation for T_{inv}:

$$a(V-b)^2 + (V-b)V^2RT - RV^3T = 0 \tag{12}$$

We get:

$$T_{inv} = \frac{2a}{Rb}\left(1 - \frac{b}{V}\right)^2 \tag{13}$$

Since we have constant enthalpy H, we know that

$$\Delta T = \left(\frac{\partial T}{\partial V}\right)\Delta V \tag{14}$$

From Equation (11) it's easy to see that at high temperature (higher than T_{inv}), the derivative is positive and for temperature lower than T_{inv} the derivative is negative. Thus, ΔT increases/decreases accordingly with positive ΔV.

One thought on “J02T.1”

December 12, 2013 at 6:53 pm

Your solution is on the right track, but sometimes it looks inconsistent. For example, your formula (9) misses one extra term coming from U (so, actually U should be not just $C_V T$), but then in (11) your expression for $(\partial H/\partial V)_?$ in the numerator looks as if you've actually included that missing term. Then (12) does NOT include the missing term again, but (13), which is claimed to follow from (12), does include the missing term (and so doesn't actually follow from (12)). One more remark about that: since you have derived F, you can easily find the correct U from it. Otherwise, why would have the author of the problem asked you to find F first?

Other remarks:
The hint in the problem didn't just give you (14) for granted, you were told that such a formula exists, but you still were supposed to derive it (the hint said ``argue that...'').
Your expression (10) has to be derived or at least explained. You should also explicitly write which variable is fixed when you take partial derivatives. So supposedly your (10) should look like $(\partial T/\partial V)_H = -\frac{(\partial H/\partial V)_T}{(\partial H/\partial T)_V}$ to be unambiguous, if that's what you mean. The same remark is true for your other formulas involving partial derivatives. E.g. it's clear that $(\partial T/\partial V)_H$ is not the same as $(\partial T/\partial V)_p$.