Easy Problem in Thermodynamics Partials

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1 Problem

Use the differential relation

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT\,, \tag{1}$$

and the following lemmas to show that

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial T}{\partial P}\right)_V^{-1}. \tag{2}$$

Lemma 1

Given that $V = V(P, T)$, then

$$\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T = 1\,, \tag{3}$$

which is presented without proof. This equation makes sense because if T is held constant then we can claim that both $V = V(P)$ and $P = P(V)$, thus (3) tells us how to take the inverse of a total derivatve.

Lemma 2: The Triple-Product Rule of Partials

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1\,. \tag{4}$$

Solution

This problem is really designed to provide you some practice manipulating the partial derivatives. Notice how similar the result of (2) is to (3), however, we're going to prove (2) the long way just for the practice.

We begin by dividing (1) by dT while keeping V constant, to get

$$\left(\frac{\partial V}{\partial T}\right)_V = \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial T}\right)_V . \tag{5}$$

Now, the term on the LHS is zero because it's attempting to differentiate a variable that's being held constant. Also, $(\partial T/\partial T)_V$ has to be equal to unity. Hence, (5) becomes

$$0 = \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_P . \tag{6}$$

Next, we multiply through by $\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T$ to get

$$0 = \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T + \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T , \tag{7}$$

which, upon invoking the Triple Product Rule, gives us

$$0 = \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T - 1 . \tag{8}$$

Using Lemma 1, the two outer factors cancel each other out, leaving us with

$$0 = \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V - 1 , \tag{9}$$

which can be solved algebraically to get

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial T}{\partial P}\right)_V^{-1} . \tag{10}$$