

FROM FEAR TO FUN IN THERMODYNAMICS: Name the Experiment (PERC 2013)

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The Activity

1. Sketch an experiment that could be used to measure the following derivative:

$$\left(\frac{\partial p}{\partial T}\right)_V$$

2. Sketch an experiment that could be used to measure the following derivative:

$$\left(\frac{\partial S}{\partial V}\right)_T$$

3. Use the differential for the Helmholtz free energy

$$dF = -SdT - pdV$$

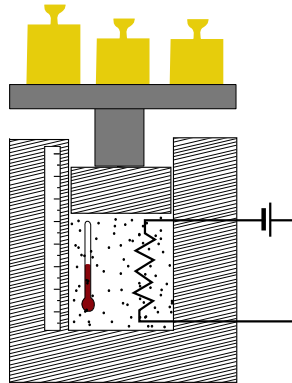
to find a mathematical relationship between these two experiments. Which experiment would be easier to perform in the lab?



Solution

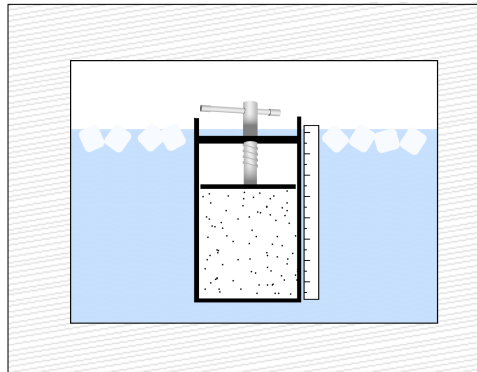
Experiment 1

The procedure involves heating the contents of an insulated piston with a resistor, and measuring how much weight needs to be added to the piston in order to return the system to its original volume.



Experiment 2

A metal piston is inserted into an insulated container of ice water with a known quantity of ice. The volume of the piston is slowly changed, and afterwards the mass of the ice is measured.



Maxwell Relation

We know the Helmholtz free energy takes form of $F = U - TS$. We are keeping the number of moles constant ($N = \text{constant}$). We know the internal energy takes form $dU = T dS - p dV$. Zapping the free energy with d , we have:

$$\begin{aligned}dF &= -p dV - S dT \\ \frac{\partial^2 F}{\partial T \partial V} &= - \left(\frac{\partial S}{\partial V} \right)_T \\ \frac{\partial^2 F}{\partial V \partial T} &= - \left(\frac{\partial p}{\partial T} \right)_V \\ \therefore \left(\frac{\partial p}{\partial T} \right)_V &= \left(\frac{\partial S}{\partial V} \right)_T\end{aligned}$$