

April 3, 2020. Exercise 2: Given the definitions below, evaluate the requested partial derivative.

$$U = x^2 + y^2 + z^2$$

$$z = \ln(y - x) + x^2$$

Find $\left(\frac{\partial U}{\partial z}\right)_y$

Working with EOSs

Thermodynamic identity

$$dU = TdS - pdV + \mu dN$$

$$U = U(S, V, N)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$$

compare

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T; \quad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -p; \quad \left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu$$

for every point on the EOS (state), the partial derivatives are numbers, and

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$$

Working with EOSs

$$U = U(x, y, z)$$

$$z = z(x, y)$$

$$dU = \left(\frac{\partial U}{\partial x} \right)_{y,z} dx + \left(\frac{\partial U}{\partial y} \right)_{x,z} dy + \left(\frac{\partial U}{\partial z} \right)_{x,y} dz$$

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

dU, dx, dy, dz are our unknowns with the partial derivatives as coefficients (just numbers)

$$dx = \frac{dz - \left(\frac{\partial z}{\partial y} \right)_x dy}{\left(\frac{\partial z}{\partial x} \right)_y}$$

$$dU = \left(\frac{\partial U}{\partial x} \right)_{y,z} \frac{dz - \left(\frac{\partial z}{\partial y} \right)_x dy}{\left(\frac{\partial z}{\partial x} \right)_y} + \left(\frac{\partial U}{\partial y} \right)_{x,z} dy + \left(\frac{\partial U}{\partial z} \right)_{x,y} dz$$

$$dU = \left(-\frac{\left(\frac{\partial U}{\partial x}\right)_{y,z} \left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y} + \left(\frac{\partial U}{\partial y}\right)_{x,z} \right) dy + \left(\frac{\left(\frac{\partial U}{\partial x}\right)_{y,z}}{\left(\frac{\partial z}{\partial x}\right)_y} + \left(\frac{\partial U}{\partial z}\right)_{x,y} \right) dz$$

$$dU = dU(y, z) = \left(\frac{\partial U}{\partial y}\right)_{x,z} dy + \left(\frac{\partial U}{\partial z}\right)_{x,y} dz$$

Already used:

$$\left(\left(\frac{\partial z}{\partial x} \right)_y \right)^{-1} = \frac{1}{\left(\frac{\partial z}{\partial x} \right)_y} = \left(\frac{\partial x}{\partial z} \right)_y$$

Today's (Monday 4/6) exercise:

Show that

$$\left(\frac{\partial x}{\partial y} \right)_f \left(\frac{\partial y}{\partial f} \right)_x \left(\frac{\partial f}{\partial x} \right)_y = -1$$

using

a) total differentials

b) explicit calculation using a triangular path (EOPC problem 3.10)

Equations of state

In thermodynamics these are empirically determined, i.e. by experiment. One goal of Statistical Mechanics is to derive these from first principles, i.e. from the fundamental laws of physics.

Ideal gas:

$$pV = Nk_B T$$

$$U = \frac{3}{2} NkT$$

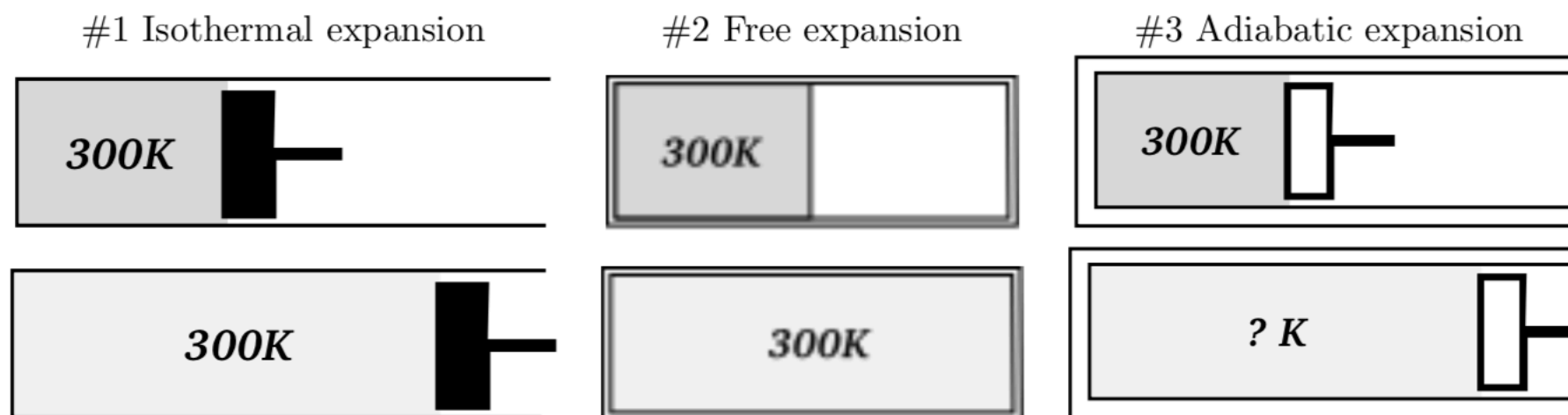
Activity: How many ways can you expand a gas in a piston?

Consider the three processes described below.

Process #1 Five moles of an ideal gas are initially confined in a one-liter cylinder with a movable piston, at a temperature of 300 K. Slowly the gas expands against the movable piston, while the cylinder is in contact with a thermal reservoir at 300 K. The temperature of the gas remains constant at 300 K while the volume increases to two liters.

Process #2 A thin plastic sheet divides an insulated two-liter container in half. Five moles of the same ideal gas are confined to one half of the container, at a temperature of 300 K. The other half of the container is a vacuum. The plastic divider is suddenly removed and the gas expands to fill the container. Because it is a free expansion of an ideal gas (no work is done on or by the gas), the final temperature of the gas is also 300 K.

Process #3 The same cylinder as in process #1 is thermally insulated and then allowed to slowly expand, starting at 300 K, to twice its original size (two liters).



1. Are $\Delta S_{\text{isothermal}}$, ΔS_{free} and $\Delta S_{\text{adiabatic}}$, the change in entropy of the gas for each process, positive, negative, or zero? Please explain your reasoning.
2. Is $\Delta S_{\text{isothermal}}$ greater than, less than, or equal to ΔS_{free} ? How do each of these compare with $\Delta S_{\text{adiabatic}}$? Please explain.
3. Are $\Delta S_{\text{surr-isothermal}}$, $\Delta S_{\text{surr-free}}$ and $\Delta S_{\text{surr-adiab}}$, the change in entropy of the surroundings for each process, positive, negative, or zero? Please explain.

Response functions

are the usual method for characterizing the macroscopic behavior of the system. They are experimentally measured from the changes of state functions with external probes.

Force constants are generalizations of the spring constant

Isothermal compressibility $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$

Magnetic susceptibility $\chi_T = \left(\frac{\partial M}{\partial B} \right)_T$

Thermal responses probe the change in state functions as a function of temperature.

Thermal expansion $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$

Heat capacities $C_x = \left(\frac{dQ}{dT} \right)_x$; $x = \{V, p\}$

Response functions

Heat capacities $C_x = \left(\frac{\cancel{dQ}}{dT} \right)_x ; \quad x = \{V, p\}$

$$C_V = \left(\frac{dQ}{dT} \right)_V = \left(\frac{dU - \cancel{dW}}{dT} \right)_V = \left(\frac{dU + p dV}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_p = \left(\frac{dQ}{dT} \right)_p = \left(\frac{dU - \cancel{dW}}{dT} \right)_p = \left(\frac{dU + p dV}{dT} \right)_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p$$

Heat capacities expressed in terms of changes in entropy:

Response functions

Heat capacities $C_x = \left(\frac{\cancel{dQ}}{dT} \right)_x ; \quad x = \{V, p\}$

$$C_V = \left(\frac{dQ}{dT} \right)_V = \left(\frac{dU - \cancel{dW}}{dT} \right)_V = \left(\frac{dU + pdV}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_p = \left(\frac{dQ}{dT} \right)_p = \left(\frac{dU - \cancel{dW}}{dT} \right)_p = \left(\frac{dU + pdV}{dT} \right)_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p$$

Heat capacities expressed in terms of changes in entropy:

$$dU = TdS - pdV \rightarrow dU + pdV = TdS$$

$$C_x = T \left(\frac{\partial S}{\partial T} \right)_x ; \quad x = \{V, p\}$$

