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Problem 4.1: Entropy differential

[**Oral** | 1 pt(s)]

ID: ex_entropy_differential:sm2324

> **Learning objective**
>
> In this exercise, we learn how to express TdS as a function of p and T, which will be useful in the next exercise "Ideal gas heat capacity"

Show that:

$$TdS = \left(\frac{\partial U}{\partial T}\bigg|_p + p\frac{\partial V}{\partial T}\bigg|_p \right) dT - T\frac{\partial V}{\partial T}\bigg|_p dp. \tag{1}$$

Hints:

- Use the exactness of $S = S(T, p)$, i.e., the fact the second derivatives are symmetrical;
- Understand the derivation of the analogous relation $TdS = \frac{\partial U}{\partial T}\Big|_V dT + T\frac{\partial p}{\partial T}\Big|_V dV$ from the script "Theorie der Wärme" by Gianni Blatter.

Problem 4.2: Ideal gas heat capacity

[**Written** | 2 pt(s)]

ID: ex_Ideal_Gas_heat_capacity:sm2324

> **Learning objective**
>
> In this exercise, we show how to express the heat capacity (at constant volume or pressure) in terms of the thermal expansion coefficient and the isothermal and adiabatic compressibility factors.

Knowing the thermal expansion coefficient $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\Big|_P$ and also isothermal and adiabatic compressibility factors (κ_T and κ_S)

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_T \text{ and } \kappa_S = -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_S, \tag{2}$$

express the heat capacity at constant volume c_V and heat capacity at constant pressure c_P in term of these coefficients.
Hints:

- Use the relation $\frac{\partial x}{\partial y}\Big|_z \frac{\partial z}{\partial x}\Big|_y \frac{\partial y}{\partial z}\Big|_x = -1$ obtained in the first problem set;
- For the subtask b), show that $\frac{c_p}{c_V} = \frac{\kappa_T}{\kappa_S}$.

a) First, as an in-between step, show that $(c_p - c_V) = TV\frac{\alpha^2}{\kappa_T}$. **1**pt(s)

b) Now, obtain the final expressions: **1**pt(s)

$$\begin{aligned} c_V &= \frac{TV\alpha^2\kappa_S}{(\kappa_T - \kappa_S)\,\kappa_T}, \\ c_P &= \frac{TV\alpha^2}{\kappa_T - \kappa_S}. \end{aligned} \tag{3}$$

Problem 4.3: Water Carnot Cycle

[**Oral** | 2 pt(s)]

ID: ex_water_Carnot_cycle:sm2324

Learning objective

The expansion coefficient of water depends on temperature. Here, we discuss how this affects the design of a Carnot engine with water as a medium.

Consider a water Carnot cycle. The coefficient of expansion is given by

$$\alpha = \frac{1}{V}\,\frac{\partial V}{\partial T}\bigg|_P, \tag{4}$$

and has the following properties, depending on the temperature of water T_w,

- if $T_w > 4°C$, then $\alpha > 0$.
- if $T_w = 4°C$, then $\alpha = 0$.
- if $T_w < 4°C$, then $\alpha < 0$.

a) Consider two water isotherms at $6°C$ and $2°C$. How must the volume change such that heat is always suplied? Use that **1**pt(s)

$$\delta Q = T\,\frac{\alpha}{\kappa_T}\,dV \tag{5}$$

and then derive this expression.
Hints:

- Show that $\delta Q = T \frac{\partial S}{\partial V}\big|_T dV$
- The isothermic compressibility $\kappa_T = -V^{-1}\,(\partial V/\partial P)_T$ is always positive because applying more pressure to a liquid does not make it larger;
- Use the exactness of the Helmholtz free energy ($dF = -S\,dT - P\,dV$) to obtain a relation between S and P. Then, express this relation using the coefficients α and κ_T.

b) Show that **1**pt(s)

$$\frac{\partial T}{\partial V}\bigg|_S = -\frac{T\,\alpha}{\kappa_T\,c_V} \tag{6}$$

and explain why it is impossible to build a Carnot cycle with the isotherms from a).
Hints:

- Consider the process in the $T - V$ diagram and calculate the slope $(\partial T/\partial V)_S$ of both adiabatic processes;
- The heat capacity at constant volume is given through $c_V = T\,(\partial S/\partial T)_V$.