

Quiz 2.4 – Exact Differentials

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Natural Variables

Write the exact differentials for the four main thermodynamic potentials (U , H , G , and A) with respect to their natural variables in two forms: (The Wikipedia page on "Thermodynamic Potentials" can be very helpful here, but Helmholtz energy is F instead of A on that page)

Showing the partial derivatives explicitly

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

$$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

Replacing the partial derivatives with the appropriate state variables

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dG = -SdT + VdP$$

$$dA = -SdT - PdV$$

Properties of Ideal gases

Find the following properties in terms of state variables (i.e. solve the derivatives) for an ideal gas:

$\alpha_T = \left(\frac{\partial U}{\partial V}\right)_T$ for an ideal gas, $U = C_V T$ and C_V is independent of V
 so $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V} \frac{\partial}{\partial T} \left. \frac{nRT}{P} \right|_P = \frac{nR}{PV} = \left(\frac{1}{T}\right)$

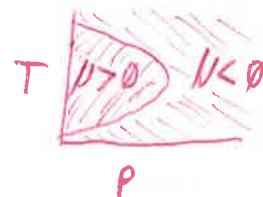
$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V} \frac{\partial}{\partial P} \left. \frac{nRT}{P} \right|_T = -\frac{nRT}{V} \cdot -\frac{1}{P^2} = \frac{P}{P^2} = \left(\frac{1}{P}\right)$

Joule-Thompson Coefficients

The Joule-Thompson coefficient is positive for most gases under most conditions. State the following:

- What conditions will lead to a negative coefficient for most gases?

Extremely high or low T , and extremely high P



- Give an example of a gas with a negative coefficient at STP

He