

4.E: Putting the First Law to Work (Exercises)

Q4.1

Given the relationship

$$\left(-\frac{\partial U}{\partial V}\right)_T = T\left(-\frac{\partial p}{\partial T}\right)_V - p \quad (4.E.1)$$

show that

$$\left(-\frac{\partial U}{\partial V}\right)_T = 0 \quad (4.E.2)$$

for an ideal gas.

Q4.2

Determine if the following differential is exact, and if so, find the function $z(x, y)$ that satisfies the expression.

$$dz = 4xy \, dz + 2x^2 \, dy \quad (4.E.3)$$

Q4.3

For a van der Waals gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{an^2}{V^2}\right) \quad (4.E.4)$$

Find an expression in terms of a , n , V , and R for

$$\left(\frac{\partial T}{\partial V}\right)_U \quad (4.E.5)$$

if $C_V = 3/2R$. Use the expression to calculate the temperature change for 1.00 mol of Xe ($a = 4.19 \text{ atm L}^2 \text{ mol}^{-2}$) expanding *adiabatically* against a vacuum from 10.0 L to 20.0 L.

Q4.4

Given the following data, calculate the change in volume for 50.0 cm³ of

- neon and
- copper

due to an increase in pressure from 1.00 atm to 0.750 atm at 298 K.

Substance	T (at 1.00 atm and 298 K)
Ne	1.00 atm ⁻¹
Cu	0.735 x 10 ⁻⁶ atm ⁻¹

Q4.5

Consider a gas that follows the equation of state

$$p = \frac{nRT}{V - nb} \quad (4.E.6)$$

derive an expression for

- the isobaric thermal expansivity, α
- the Joule-Thomson coefficient, μ_{JT}

$$\mu_{JT} = \frac{V}{C_p}(T\alpha - 1) \quad (4.E.7)$$

Q4.6

Given

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V \quad (4.E.8)$$

derive an expression for

$$\left(\frac{\partial U}{\partial p}\right)_T \quad (4.E.9)$$

in terms of measurable properties. Use your result to calculate the change in the internal energy of 18.0 g of water when the pressure is increased from 1.00 atm to 20.0 atm at 298 K.

Q4.7

Derive an expression for

$$\left(\frac{\partial U}{\partial T}\right)_p \quad (4.E.10)$$

Begin with the definition of enthalpy, in order to determine

$$dH = dU + pdV + Vdp \quad (4.E.11)$$

Finish by dividing by dT and constraining to constant pressure. Make substitutions for the measurable quantities, and solve for

$$\left(\frac{\partial U}{\partial T}\right)_p. \quad (4.E.12)$$

Q4.8

Derive an expression for the difference between C_p and C_V in terms of the internal pressure, α , p and V . Using the definition for H as a starting point, show that

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \quad (4.E.13)$$

Now, find an expression for by starting with $U(V, T)$ and writing an expression for the total differential $dU(V, T)$.

Divide this expression by dp and constrain to constant T . Substitute this into the previous expressions and solve for

$$\left(\frac{\partial G}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V. \quad (4.E.14)$$

Q4.9

Evaluate the expression you derived in problem 8 for an ideal, assuming that the internal pressure of an ideal gas is zero.

Contributors and Attributions

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