

CHEM 3410: Physical Chemistry I — Fall 2009

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Lecture 4: More on working with the first law: ideal gases and internal energy

References

1. Levine, *Physical Chemistry*, Sections 2.4–2.6, 2.8–2.9

Key Concepts

- We “derived” another way to define the constant volume heat capacity: $\left(\frac{\partial U}{\partial T}\right)_V = C_V$
- A similar result for the constant pressure heat capacity: $\left(\frac{\partial H}{\partial T}\right)_P = C_P$
- For an ideal gas **only** the internal energy and enthalpy are only a function of temperature. Mathematically, this can be written as:

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial H}{\partial V}\right)_T = 0$$

This should make physical sense based on the assumption that for an ideal gas, the gas atoms and molecules are non-interacting. If there is no interaction, changing how close together the atoms or molecules are will not change their energy. In this case, temperature is the only parameter that has an impact on the internal energy or enthalpy.

- Since both internal energy and enthalpy are state functions, we can always construct an isothermal path to calculate the changes in these thermodynamic potentials for an ideal gas.
- So, for an ideal gas, regardless of the path of a process, the change in internal energy is completely determined by the initial and final temperatures:

$$\Delta U(\text{ideal gas}) = \int_{T_1}^{T_2} C_v dT$$

and if the heat capacity is a constant over this temperature range this reduces to:

$$\Delta U(\text{ideal gas}) = C_v(T_2 - T_1) = C_v\Delta T$$

The common misunderstandings here are: (1) this only works for an ideal gas where U is independent of temperature and (2) even though the actual process is not constant volume, we can still use this approach because U is a state function and is only a function of T .

- A similar argument can be developed for enthalpy. For any process involving an ideal gas:

$$\Delta H(\text{ideal gas}) = \int_{T_1}^{T_2} C_p dT$$

Related Exercises in Levine

Exercises 2.27, 2.40, 2.45