

Chemistry 331

Lecture 12 Heat Capacity State and Path Functions

NC State University

Question

Which expression correctly gives the work of expansion ($V_2 > V_1$)?

- A. $nRT \ln \left(\frac{V_2}{V_1} \right)$
- B. $-nRT \ln \left(\frac{V_2}{V_1} \right)$
- C. $nR \ln \left(\frac{V_2}{V_1} \right)$
- D. $-nR \ln \left(\frac{V_2}{V_1} \right)$

The measurement of heat

We must carefully distinguish between heat and temperature. When we add heat to the system its temperature increases. We can use measurement of the temperature to determine how much heat has been added. However, we need to know the heat capacity of the system in order to do this.

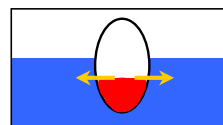
$$\text{Heat capacity} = \frac{\text{Heat supplied}}{\text{Temperature rise}}$$

The heat capacity is called C. If we perform a heat exchange at constant volume then we designate the heat capacity as C_V . If the process occurs at constant pressure we call the heat capacity C_P .

$$C_{V,P} = \frac{q_{V,P}}{\Delta T}$$

Calorimetry

The science of heat measurement is called calorimetry. A calorimeter consists of a container in a heat bath. A physical or chemical process occurs in the container and heat is added or removed from the heat bath. The temperature increases or decreases as result. By knowing the heat capacity of the bath we can measure the amount of heat that has been added or removed from the system.



Energy in the form of heat flows into the bath.

Calorimetry

In the studies of biological systems there are two important types of calorimetry.

1. Differential scanning calorimetry (DSC)
2. Isothermal titration calorimetry (ITC)

In DSC the temperature is increased at a constant heating rate and the heat capacity is measured. DSC is used for determining the parameters associated with phase transitions e.g. protein unfolding, denaturation, DNA hybridization etc.

In ITC the temperature is held constant while one component is added to another. The heat of interaction (e.g. binding) is measured using this method. ITC is widely used to determine the enthalpy of binding, e.g. for protein-protein and protein-drug interactions among other types of biological applications.

Molar and Specific Heat Capacities

We use molar heat capacities for pure substances. As the name implies the units are J/mol-K for the molar heat capacity. We write the molar heat capacity at constant volume as $C_{V,m}$.

For mixtures we cannot use a molar heat capacity and so we use the specific heat capacity, which is the heat capacity per gram of material with units of J/g-K.

Calculating the internal energy change

We have seen that the internal energy depends only on temperature. For example, for a change of pressure (and temperature) at constant volume we saw that $\Delta U = q_v$ since the work is zero for a constant volume process.

Thus, at constant volume:

$$\Delta U = q_v = C_v \Delta T$$

But, in fact when we consider the origin of the internal energy in the kinetic theory of gases we realize that:

$$\Delta U = \frac{3}{2} n R \Delta T = C_v \Delta T$$

and therefore:

$$C_v = \frac{3}{2} n R \quad \text{and} \quad C_{v,m} = \frac{3}{2} R$$

The heat capacity at constant pressure

For a constant pressure step we saw in the last lecture that:

$$q_p = q_v + P \Delta V$$

By analogy with the constant volume process:

$$q_p = C_p \Delta T$$

and therefore:

$$C_p \Delta T = C_v \Delta T + P \Delta V$$

$$C_p \Delta T = C_v \Delta T + n R \Delta T$$

$$C_p = C_v + n R$$

$$\text{so that } C_p = \frac{5}{2} n R \quad \text{and} \quad C_{p,m} = \frac{5}{2} R$$

Definition of the enthalpy

Based on these considerations we can see that there is a new state function, the energy at constant pressure. This state function is known as the enthalpy H . The enthalpy change is:

$$\Delta H = q_p = C_p \Delta T$$

and we can rewrite the relationship from the previous slide as:

$$\Delta H = \Delta U + P \Delta V$$

We have also defined the relationship between the internal energy and the enthalpy. The $P \Delta V$ term represents the work of expansion (or compression) done against the atmosphere during a chemical reaction. We use enthalpy instead of internal energy under normal conditions because it includes this work automatically.

Heat Capacity for a Diatomic Molecule

For a diatomic molecule there is contribution from rotations as well as translations. This means that as heat is added to the system the rotational levels can be populated in addition to an increase in molecular speed. The kinetic theory of gases considers only the speed. An approximate rule is that we obtain a contribution to the heat capacity, C_v of $1/2 n R$ for each degree of freedom. We saw that for a monatomic gas the heat capacity was $C_v = 3/2 n R$. A diatomic gas has two rotational degrees of freedom and so the heat capacity is approximately $C_v = 5/2 n R$. What does this say about C_p ? Well, the relationship between C_p and C_v holds for all gases so $C_p = 7/2 n R$ for a diatomic "ideal" gas.

Question

What is the internal energy of a monatomic gas?

- A. $U = \frac{3}{2} R$
- B. $U = \frac{3}{2} R T$
- C. $U = \frac{3}{2} n R$
- D. $U = \frac{3}{2} n R T$

Question

If the heat capacity of a diatomic gas is $5/2 n R$, what is the internal energy of a diatomic ideal gas?

- A. $U = \frac{5}{2} R$
- B. $U = \frac{5}{2} n R T$
- C. $U = \frac{3}{2} n R$
- D. $U = \frac{3}{2} n R T$

Adiabatic Processes

If a process occurs in an isolated system then no heat can be transferred between the system and surroundings. In this case the heat transferred, q , is zero, i.e. $q = 0$. Therefore,

$$\Delta U = w$$

We call such processes adiabatic.

Actually, this special case is of great importance. For example, when a column of air rises in the atmosphere it expands and cools adiabatically. Expressed in differential format:

$$\begin{aligned} dU &= \delta w \\ C_V dT &= -PdV \end{aligned}$$

Here we have used the definitions of the internal energy in terms of the heat capacity and the work in pressure-volume terms.

Adiabatic Processes

Using the form on the previous page we can derive the relationship between the volume change and temperature.

$$\begin{aligned} dU &= \delta w \\ C_V dT &= -PdV \\ C_V dT &= -\frac{nRT}{V} dV \\ C_V \frac{dT}{T} &= -nR \frac{dV}{V} \\ C_V \int_{T_1}^{T_2} \frac{dT}{T} &= -nR \int_{V_1}^{V_2} \frac{dV}{V} \\ C_V \ln\left(\frac{T_2}{T_1}\right) &= -nR \ln\left(\frac{V_2}{V_1}\right) \end{aligned}$$

Adiabatic Processes

Using the form on the previous page we can derive the relationship between the volume change and temperature.

$$\ln\left(\frac{T_2}{T_1}\right) = \frac{nR}{C_V} \ln\left(\frac{V_1}{V_2}\right)$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{nR/C_V}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{2/3} \text{ for an ideal monatomic gas}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{2/5} \text{ for an ideal diatomic gas}$$

This expression is great practical value since you can predict the temperature of air as it rises. This phenomenon leads to rain over mountains and cooling that affects ecosystems at high elevation.

Question

Which statement is true for an adiabatic compression?

- A. $\Delta U = q$
- B. $\Delta U = q + w$
- C. $\Delta U = w$
- D. $\Delta U = q - w$

Question

Which statement is true for an adiabatic expansion?

- A. The temperature increases as gas expands
- B. The temperature decreases as gas expands
- C. The temperature remains constant
- D. The work done is equal to the heat transferred

Path Functions

We have seen that work and heat are path functions. The magnitude of the work and heat depends not just on the final values of the T and P , but also on the path taken.

We can summarize the paths and their implications in the table below.

Path	Condition	Result
Isothermal	$\Delta T = 0$	$w = -q$
Constant V	$\Delta V = 0$	$w = 0, \Delta U = C_V \Delta T$
Constant P	$\Delta P = 0$	$w = -P\Delta V, q_P = C_P \Delta T$
Adiabatic	$q = 0$	$\Delta U = w$

State Functions

At present we have introduced two state functions:

Internal Energy ΔU

Enthalpy ΔH

State functions do not depend on the path, only on the value of the variables.

We can make the analogy with elevation. The potential energy at an elevation h , which we call $V(h)$ does not depend on how we got to that elevation. If we compare $V(h_1)$ in Raleigh to $V(h_2)$ on Mt. Mitchell the difference $V(h_2) - V(h_1)$ is the same regardless of whether we drive to Mt. Mitchell through Statesville or Asheville. The work we do to get (i.e. how much gas we use in a car!) is a path function.

Question

Enthalpy is a state function, therefore it depends only on

- A. the temperature and pressure
- B. the elevation
- C. the work of expansion in a reaction
- D. the volume