

## Lecture 1: State Variables

Syllabus is on the web. My web address is in my email signature. If you did not receive an email message from me, contact me at [rjgordon@uic.edu](mailto:rjgordon@uic.edu) immediately.

Office hours every day Monday through Thursday. Let me know if these are insufficient or inconvenient.

Second session on Friday will deal mainly with problem solving, but new material may also be presented. Attendance is required. The first few Fridays will end early, and in those weeks there will not be any break between sessions.

The course will cover the first nine chapters of Atkins. See the syllabus and calendar for further details.

Physical chemistry is difficult because it draws from many areas of chemistry and physics. It requires a knowledge of classical mechanics, thermodynamics, electricity and magnetism, quantum mechanics, statistical mechanics, as well as chemistry. It is also very problem oriented.

Tips on how to solve problems:

1. Do *not* use a calculator or computer until the very end. Keep the solution as analytical as possible.
2. Keep track of the dimensions of the variables. Try to use dimensionless variables as much as possible.
3. When you do get a numerical answer, judge whether it has a physically realistic size and proper units.

## Scope of the Course

*Chemistry 342*: A central problem of 19<sup>th</sup> century physics: understanding the **macroscopic** states of matter and their transformations (e.g., phase transitions, chemical reactions, equilibrium, kinetics). The link to the microscopic world is through the kinetic theory of gases.

*Chemistry 344*: A central problem of 20<sup>th</sup> century physics: understanding the **microscopic** properties of matter and deriving from them the macroscopic observables; relating chemical structure, spectroscopy, and kinetics to quantum mechanics.

Q. How do we describe the macroscopic state of matter?

A. By a list of *state variables*. By definition, such variables do not depend on the previous history of the system. Compared with the microscopic  $\sim 10^{25}$  variables needed to describe the system, only a few are needed to describe a macroscopic object. Our goal is to identify these variables and the physical laws that relate them.

There are two types of state variables: *extensive* ones and *intensive* ones.

Think of a swimming pool.

### Examples of Extensive Variables

Number of moles of each chemical component:  $n_1, n_2, \dots, n_r$ . These are dimensionless quantities. Knowing them is equivalent to knowing the mass of the system.

Energy of the system:  $U$  ( $\text{kg m}^2 \text{s}^{-2}$ ; joules)

There are different sources of energy. Kinetic energy can come from internal motions of a molecule or crystal, such as vibration, bending, and torsional motion. Kinetic energy can also come for external motion, such as translation and rotation. Potential energy can come from electronic energy, and contributes to the chemical energy of a system. They all add up to the total energy,  $U$ . Understanding the different types of energy and their interconversions is a major topic of this course.

Volume:  $V$  ( $\text{m}^3$ )

Magnetic dipole moment:  $I$  (joules/Tesla)

Electric dipole moment:  $\mu$  (C m)

Length (of a rubber band, polymer):  $L$  (m)

Surface area (bubble, droplet):  $A$  ( $\text{m}^2$ )

Entropy:  $S$ , a measure of disorder or chaos. It is dimensionless.

### Examples of Intensive Variables

Pressure:  $P$ . Defined as the force per unit area:  $\text{Newtons/m}^2 = \text{pascal}$

Temperature:  $T$ . Definition is complicated. Think of it for now as proportional the translational energy per particle. (Hotter particles move faster.) It has the dimensions of energy.

Chemical Potential:  $\mu_i$ , chemical energy per mole of substance  $i$  (joules)

Magnetic field,  $B$  (Tesla)

Electric field:  $E$  (Volts/m)

Tension,  $T_L$  (joules/m)

Surface tension:  $\gamma$  (Joules/m<sup>2</sup>)

### Relation between extensive and intensive variables:

$P$  and  $V$ : Applying pressure to an object reduces its volume.

$$PV = (\text{newtons/m}^2) \text{ m}^3 = \text{force} \times \text{distance} = \text{joules}$$

$$\mu_i n_i = (\text{joules/mole}) \text{ number of moles} = \text{joules}$$

$$IB = (\text{joules/tesla}) \text{ tesla} = \text{joules}$$

$$\mu E = (\text{Cm}) \text{ V/m} = CV = \text{Joules}$$

$$T_L L = (\text{J/m}) \text{ m} = \text{Joules}$$

$$\gamma A = (\text{Joules/m}^2) \text{ m}^2 = \text{Joules}$$

The tricky case is temperature. The extensive variable associated with temperature is entropy.

$$TS = \text{joules}$$

### The Euler Relation

$$U = TS - PV + \sum_i \mu_i n_i + IB + \mu E + T_L L + \gamma A + \dots$$

What we have done is replace the myriads of variables needed to describe the microscopic system with just a handful of macroscopic state variables. For example, we do not care about the charge on each particle, just the overall dipole moment of the bulk sample. If we need greater precision, we might specify also the quadrupole moment, as well as some higher multipole moments, but the list is still short.

But not all macroscopic variables are state variables. Example of a swimming pool that can be filled with either rain water or water from the faucet. There is no way of telling from the present state of the pool how much of each was used to fill the pool. All we can say is that the sum of the two sources equals the total water content of the pool:

$$\text{Water} = \text{Water}_{\text{rain}} + W_{\text{faucet}}$$

Similarly, the energy content of a thermodynamic system is the sum of work done on the system (ordered energy input) and heat added to the system (chaotic energy):

$$U = w + q$$

The size of  $w$  and  $q$  individually depends on the path taken (history of the system) and not on the state of the system.

## Lecture 2: Ideal Gas Law

Assumptions of an ideal gas:

1. Particles are point masses
2. No forces between the particles (elastic collisions)

We will check these assumptions later.

### Relation Between State Variables T,P, n, V

$m$  = mass of one particle

$V$  = volume of chamber

$\rho_n$  = number density = number of particles/ $V$

=  $n N_A/V$  ( $N_A$  = Avogadro's number)

$A$  = area of wall

$v$  = velocity of particle in one dimension

$p_{in}$  = momentum of particle striking the wall =  $mv$

$p_{final}$  = momentum of particle bouncing off the wall =  $-mv$

$\Delta p$  = momentum change =  $2mv$

In time  $\Delta t$ , a particle moves a distance  $v\Delta t$ .

Half of the particles in a volume  $Av\Delta t$  strike the wall in time  $\Delta t$ . (The other half are moving in the wrong direction.)

$\Delta p_{wall}$  = Total momentum imparted to the wall in time  $\Delta t$  =  $(2mv) (\rho_n/2) (Av\Delta t)$

=  $mv^2 n N_A A \Delta t / V$

Force =  $\Delta p_{wall} / \Delta t$  =  $mv^2 n N_A A / V$

Pressure on wall =  $P$  = Force/Area =  $mv^2 n N_A / V$

$$PV = n N_A m v^2$$

$\frac{1}{2} m v^2$  = kinetic energy of one particle

$\frac{1}{2} N_A m v^2$  = kinetic energy of one mole particles = constant times  $T$  =  $RT$

$$PV = nRT$$

This is the equation of state of an ideal gas.

We define Boltzmann's constant as  $k=R/N_A$ , so that  $PV = nN_A kT$ .

The problem is more complicated because the particles don't all have the same speed and they don't all move in one dimension, but the proportionality  $PV \sim nT$  still holds.

$R$  is called the gas constant. Its units are

$\text{L atm mol}^{-1} \text{K}^{-1}$  from  $PV=nRT$

$\text{J mol}^{-1} \text{K}^{-1}$  from  $U \propto RT$

How good is assumption 1?

Suppose the radius of a molecule is  $3 \times 10^{-8}$  cm. For 1 mole at 1 atm at 298 K, the volume of the molecules is

$$V_0 = (4/3) \pi r^3 N_A = 68 \text{ cm}^3 = 0.068 \text{ l.}$$

If the gas pressure is 1 atm,<sup>1</sup> its volume is

$$V = nRT/P = 1 \times 0.08206 \times 298/1 = 24.4 \text{ l.}$$

The error fractional introduced by assuming point masses =  $V_0/V = 0.0028$ .

Clearly, we can make the error much smaller by reducing  $P$ .

One way of defining the temperature is by the equation of state of a very dilute gas.

Suppose a fixed volume of gas,  $V$ , is in thermal equilibrium with some standard system, such as water at its triple point.<sup>2</sup>

Let the pressure of the gas be  $P_3$ .

We define the absolute temperature of the triple point to be some number,  $\theta_3$ . (In this case, 273.16 K.)

Under some other condition (for example, the gas thermometer might be in thermal equilibrium with boiling water), the same mass and volume of gas has a pressure  $P$ . The absolute temperature of the gas in that case is then given by the ideal gas law:

$$\theta(P) = (P/P_3)\theta_3.$$

$\theta(P)$  means that  $\theta$  is a function of  $P$ .

To guarantee that the gas has ideal behavior, we take a limit,

$$\theta(P) = \lim_{(P, P_3 \rightarrow 0)} (P/P_3)\theta_3.$$

We can also define the absolute temperature in terms of two fixed points, such as the melting and boiling points of water. We arbitrarily divide the temperature interval into 100 parts. Again assume a fixed mass and volume of gas, and define the two absolute temperatures to be  $\theta_0$  and  $\theta_{100}$ .

The absolute temperature at some arbitrary condition is given by:

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<sup>1</sup> 1 atmosphere = 1.01325 bar = 101,325 pascal = 760 Torr

<sup>2</sup> Triple point of H<sub>2</sub>O: 6.11 mbar, 273.16K

$$(\theta(P) - \theta_0)/100 = (P - P_0)/(P_{100} - P_0).$$

Again, take the limit of  $P_0 \rightarrow 0$ .

We define the Celsius temperature,  $T$ , by

$$T = \theta - \theta_0.$$

**Note:** In the water example, it is an arbitrary choice to define  $\theta_0 = 273.15$  K and  $\theta_{100} = 373.15$  K. These choices are unique to the Kelvin scale. An alternative is given in problem 1.3. What all absolute temperature scales have in common is that  $\theta \rightarrow 0$  in the limit that  $PV \rightarrow 0$ .

**Note:** An absolute temperature scale could also be devised by using a fixed pressure and allowing the volume to change when the thermometer comes into contact with the various heat baths. In this case we would use the notation  $\theta(V)$ . In all of these examples, we use one or two large heat baths as references to define the temperature scale, and we use the gas sample as a thermometer.

### How is pressure measured?

**Principle of the manometer:** Compare the pressure of the sample with the force of gravity.

Let  $P$  be the pressure of the unknown gas.

Let  $\rho$  be the mass density of the fluid in the manometer.

Let  $h$  be the height difference of the fluid in the two arms of the manometer.

Let  $A$  be the cross sectional area of the arms.

The force exerted by the gas on the fluid in one arm of the manometer is  $PA$ .

Additional force exerted by the fluid in the evacuated arm of the manometer is  $\Delta mg$ , where  $\Delta m$  is the mass difference of the fluid in the two arms.

But  $\Delta m = \rho Ah$ , giving a force of  $\rho Ahg$ .

Therefore  $PA = \rho Ahg \Rightarrow P = \rho gh$

### Buoyancy

Why does a cork float?

Let  $h$  be the height of the cork, and  $A$  its cross sectional area. Its volume is  $V = hA$ .

The pressure difference is from the top to the bottom of the cork is:  $\Delta P = \rho_{\text{medium}}gh$ .

The force difference is:

$$\Delta F = \rho_{\text{medium}}ghA = \rho_{\text{medium}}gV.$$

Gravitational force on the cork  
 $= -m_{\text{cork}}g = -\rho_{\text{cork}}gV.$

Net upward force on the cork

$$F = (\rho_{\text{medium}} - \rho_{\text{cork}})gV.$$

How does a balloon work?

Refer to the accompanying diagram.

The radius of the balloon is  $r$ .

The height above the “equator” is  $h=r \cos\theta$

The pressure difference on an infinitesimal ribbon above and below the equator is

$$\Delta P = \rho_{\text{air}}g(2h)$$

The vertical force difference on the ribbon is

$$\Delta F = \rho_{\text{air}}g(2h)\cos\theta \{ (2\pi r \sin\theta) r d\theta \}$$

Integrating over the entire surface of the balloon:

$$\Delta F = \int_0^{\pi/2} 2\rho_{\text{air}}gr \cos^2\theta (2\pi r^2 \sin\theta) d\theta = 4\pi\rho_{\text{air}}gr^3 \int_0^{\pi/2} \cos^2\theta \sin\theta d\theta$$

=

$$4\pi\rho_{\text{air}}gr^3 \int_0^1 x^2 dx = \frac{4}{3}\pi r^3 \rho_{\text{air}}g = V\rho_{\text{air}}g = m_{\text{air}}g$$

Subtracting the force on the gas inside the balloon,

$$\Delta F = (\rho_{\text{air}} - \rho_{\text{gas}}) Vg$$

Gas Mixtures: Dalton’s Law

Suppose there are  $n_1$  moles of substance 1 and  $n_2$  moles of substance 2 present.  
 $V$  and  $T$  are the same for both substances.

$$P_1V = n_1RT \text{ and } P_2V = n_2RT$$

or

$$P_1 = n_1RT/V = (n_1/(n_1+n_2)) nRT /V = x_1P$$

Similarly, for any component  $i$ , with mole fraction,  $x_i$ ,

$$P_i = x_i P$$

**Question:** A certain gas has a pressure 300 Torr and consists of 1 gram of  $H_2$  and 1 gram of He. What are the partial pressures of each component?

**Question:** (Exercise 1.10). The density of air at 740 Torr and 27°C is 1.146g/l. Assuming that air consists only of N<sub>2</sub> and O<sub>2</sub>, what are their mole fractions and partial pressures?

### Lecture 3. Kinetic Theory of Gases, Part I

#### Discrete probability distributions

Example of size distribution of words in a text

Number of letters, L <sub>i</sub>	1	2	3	4	5	6	7
Frequency	5	10	17	8	2	0	1
Probability	5/43	10/43	17/43	8/43	2/43	0	1/43

$$p_i = n_i/N$$

$$N = \sum n_i$$

$$\langle L \rangle = \sum L_i P_i = 1 \times 5/43 + 2 \times 10/43 + \dots + 7 \times 1/43 = 2.9$$

$$\langle L^2 \rangle = \sum L_i^2 P_i = 1 \times 5/43 + 4 \times 10/43 + \dots + 49 \times 1/43 = 9.9$$

$$L_{\text{rms}} = (9.9)^{1/2} = 3.1$$

Most probable length = 3

#### Continuous distributions

$f(v)dv$  is the probability of observing a speed between  $v$  and  $v+dv$ .

$f(v)$  is the probability density. What are its dimensions?

$$\text{Normalization: } \int_{-\infty}^{\infty} f(v)dv = 1$$

**Warning:** Be careful to use the correct limits of integration. They are not necessarily  $\pm\infty$ .

$$\text{Probability of observing a speed between } v_1 \text{ and } v_2 : P(v_1, v_2) = \int_{v_1}^{v_2} f(v)dv$$

Most probable speed:  $df/dv=0$

Mean speed:  $\langle v \rangle = \bar{v} = \int_{-\infty}^{\infty} v f(v) dv$

RMS speed:  $v_{rms} = \left\{ \int_{-\infty}^{\infty} v^2 f(v) dv \right\}^{1/2}$

### One-dimensional Maxwell-Boltzmann distribution

$$f(v) = C \exp\{-1/2 mv^2/kT\} = C \exp\{-v^2/\alpha^2\}$$

where  $1/2 m\alpha^2 = kT$  and  $m$  is the atomic mass

$\alpha \approx$  speed sound  $\approx 400$  m/s

Define the **dimensionless variable**:  $x \equiv v/\alpha$

$$f(x) = C \exp(-x^2)$$

Normalization:  $C \int_{-\infty}^{\infty} e^{-x^2} dx = C\sqrt{\pi} = 1$

$$f(v) = (1/\alpha\pi^{1/2}) \exp(-v^2/\alpha^2)$$

Note the limits of integration.

Most probable velocity is zero.

Average velocity is also zero because

$$\int_{-\infty}^{\infty} x e^{-x^2} dx = 0$$

Root mean square velocity:

$$\langle v^2 \rangle = \frac{1}{\alpha\sqrt{\pi}} \int_{-\infty}^{\infty} v^2 e^{-v^2/\alpha^2} dv = \frac{\alpha^2}{\sqrt{\pi}} \int_{-\infty}^{\infty} x^2 e^{-x^2} dx = \frac{\alpha^2}{2}$$

$$v_{rms} = \alpha/2^{1/2}$$

$$1/2 m \langle v^2 \rangle = 1/4 m \alpha^2 = 1/2 kT = \langle E \rangle$$

### Lecture 4: Kinetic Theory of Gases, Part II

#### Three-dimensional distribution

$$f(v_x, v_y, v_z) dv_x dv_y dv_z = f(v_x) f(v_y) f(v_z) dv_x dv_y dv_z$$

$$= C^3 \exp\{-(v_x^2 + v_y^2 + v_z^2)/\alpha^2\} dv_x dv_y dv_z$$

$$v^2 = v_x^2 + v_y^2 + v_z^2; \quad x^2 = v^2/\alpha^2$$

$$dv_x dv_y dv_z = v^2 \sin\theta \, d\theta \, d\phi$$

Take the average over all angles. What remains is

$$f(x) = C x^2 \exp(-x^2), \text{ where } 0 \leq v \leq \infty$$

$$\text{Normalization: } \int_0^{\infty} x^2 e^{-x^2} dx = \sqrt{\pi} / 4$$

**Note** the limits of integration.

$$f(v) = (4/\alpha^3 \pi^{1/2}) v^2 \exp \{-v^2/\alpha^2\}$$

$$\text{Note: } x^2 dx = v^2 dv / \alpha^3$$

Most probable speed:

$$df/dx = 0 \Rightarrow x_{mp} = 1 \Rightarrow v_{mp} = \alpha$$

$$\text{Average speed: } \langle x \rangle = \frac{4}{\sqrt{\pi}} \int_0^{\infty} x^3 e^{-x^2} dx = \frac{2}{\sqrt{\pi}}$$

$$\langle v \rangle = (2/\pi^{1/2}) \alpha$$

**Show that**  $\frac{1}{2} m \langle v^2 \rangle = 3/2 kT = \langle E \rangle$ . This a further example of the Equipartition Theorem.

**Question:** What fraction of the molecules have speeds greater than  $v_0$ ?

$$\text{Answer: } \int_{v_0}^{\infty} f(v) dv = \frac{4}{\sqrt{\pi}} \int_{x_0}^{\infty} x^2 e^{-x^2} dx$$

$$\text{Integrate by parts: } \quad u=x, \, dv = x \exp(-x^2) dx, \\ \quad \quad \quad du=dx, \, v = -(1/2) \exp(-x^2)$$

$$\text{Result: } \frac{2x_0}{\sqrt{\pi}} e^{-x_0^2} + \frac{2}{\sqrt{\pi}} \int_{x_0}^{\infty} e^{-x^2} dx = \frac{2}{\sqrt{\pi}} e^{-x_0^2} + 1 - \text{erf}(x_0)$$

The **error function** is defined on page 329.

**Question:** In two dimensions, the same analysis shows the speed distribution is proportional to  $v \exp(-v^2/\alpha^2)$ . What is the most probable speed, and what is the probability of finding a speed greater than this value?

## Kinetic Theory of Collisions

Collision frequency:

Let molecules A and B have radii  $r_a$  and  $r_b$ .

Suppose molecule B is stationary, and A moves with an average speed  $\langle v \rangle$ .

Area swept out by A is  $\pi(r_a+r_b)^2 = \sigma_{ab}$ .

$\sigma_{ab}$  is the collision cross section. In general, it is the *effective* target area, and may be energy dependent.

Volume swept out by A in one second is  $\sigma_{ab}\langle v \rangle$ .

Number of collisions experienced by one A molecule in one second is

$$z_{ab} = \sigma_{ab} \langle v \rangle (n_b/V) N_A = \sigma_{ab} \langle v \rangle \mathcal{N}_b$$

where  $\mathcal{N}_b$  is the number density of B.

Equivalently,

$$\sigma_{ab} \langle v \rangle (P_b/RT) N_A = \sigma_{ab} \langle v \rangle (P_b/k_B T).$$

Dimensions are  $\text{sec}^{-1}$ .

For  $\sigma_{ab} = 100 \text{ \AA}^2 = 1 \text{ nm}^2$ ,  $P_b = 1 \text{ Torr} = 133 \text{ pa}$ ,  
 $\langle v \rangle = 400 \text{ m/s}$ ,  $T=300\text{K} \Rightarrow z_{ab} \sim 10^7 \text{ s}^{-1}$ ,  
or 10 collisions / $\mu\text{s/Torr}$ .

For constant volume,  $z_a \sim T^{1/2}$

$$\text{Average speed} = \langle v \rangle = \sqrt{\frac{4}{\pi}} \alpha = 145.5 (T/M_{\text{amu}})^{1/2} \text{ m/s}$$

The total number of collisions between species A and species B per second per unit volume is

$$\begin{aligned} Z_{AB} &= z_{ab} (n_a/V) N_A = \sigma_{ab} \langle v \rangle N_A^2 (n_a/V) (n_b/V) \\ &= \sigma_{ab} \langle v \rangle N_A^2 c_a c_b \end{aligned}$$

The number of moles of A that react per  $\text{m}^3$  per second is  $\sigma_{ab} \langle v \rangle N_A c_a c_b$

The rate constant is  $k(T) = \sigma_{ab} \langle v \rangle N_A = 2.4 \times 10^8 \text{ m}^3/\text{mole}/\text{sec} = 2.4 \times 10^{14} \text{ cm}^3/\text{mole}/\text{sec}$   
 $= 4 \times 10^{-10} \text{ cm}^3/\text{molecule}/\text{sec}$ .

This is the rate constant for **elastic collisions**. Chemical reactions are generally much slower.

Proper average over scattering angles introduces a factor of  $\sqrt{2}$ .

Proper average over speeds gives the rate constant  $k(T) = \int \sigma(v)vf(v)dv$ .

### Mean Free Path

The time between collisions is  $1/z_{ab}$ . The distance a molecule travels between collisions is

$$\lambda = \langle v \rangle / z_{ab} = (2^{1/2} \sigma_{ab} N_b)^{-1}$$

In liquid water, assume  $\sigma \approx 0.5 \times 10^{-18} \text{ m}^2$   
 $c = 1/18 \text{ moles/cm}^3 = 3.35 \times 10^{28} \text{ molecules/m}^3$   
 $\lambda = 0.42 \times 10^{-10} \text{ m} = 0.42 \text{ \AA}$

For 1 Torr  $\text{N}_2$ , 298 K,  $\sigma = 0.42 \text{ nm}^2$ ,  
 $c = 5.4 \times 10^{-5} \text{ moles/liter}$ ,  $N = 3.24 \times 10^{22} \text{ molecules/m}^3$ ,  $\lambda = 5.2 \times 10^{-5} \text{ m} = 5.2 \times 10^5 \text{ \AA}$

### Rough rule of thumb:

$$\lambda = 1000 \text{ Angstroms at } 1000 \text{ Torr.}$$

The previous result is within a factor of two of the rule.

How low must the pressure of  $\text{N}_2$  be to have  $\lambda = 1 \text{ m}$ ?  
 $N = 1.7 \times 10^{22} \text{ molecules/m}^3 \Rightarrow P = 5 \times 10^{-5} \text{ Torr.}$

### Effusion

The leak rate through a pinhole is given by the flux of molecules through the hole. The volume swept out in one second is  $A \langle v \rangle$ . The number of molecules in that volume is  $N \langle v \rangle A$ . The number of molecules hitting the area  $A$  is approximately

$$\Gamma = n \langle v \rangle / 2 \text{ m}^{-2} \text{ sec}^{-1}$$

More rigorous treatment:

$$\Gamma = n \int (v \cos \theta) f(\vec{v}) d^3 \vec{v} = n \iiint (v \cos \theta) f(v) v^2 \sin \theta d\theta d\phi dv$$

Note: volume of the parallelepiped of molecules striking the surface per second is  $v \cos \theta A$ .

$$\Gamma = n \alpha^3 \pi^{-3/2} \int_{v=0}^{\infty} v^2 dv \int_{\theta=0}^{\pi/2} \sin \theta d\theta \int_{\phi=0}^{2\pi} d\phi v \cos \theta e^{-v^2/\alpha^2}$$

Note: Integral over angles is  $\pi$ .

$$\Gamma = n\alpha\pi^{-1/2} \int_0^{\infty} x^3 e^{-x^2} dx = n\langle v \rangle / 4$$

Result: rate of effusion =  $N\langle v \rangle / 4$

Number of molecules passing through a hole of area A in one second is  $N\langle v \rangle A / 4$ .

Suppose the pressure is  $10^{-5}$  Torr. How long does it take to form a monolayer coating of  $N_2$  at 298 K, assuming  $\sigma = 0.4 \text{ nm}^2$ ?

Number of molecules per  $\text{m}^2$  is  $1/\sigma = 2.5 \times 10^{18}$   
 $N = 3.24 \times 10^{17} \text{ m}^3$ ,  $\langle v \rangle = 475 \text{ m/s}$

$$3.24 \times 10^{17} t \times 475 / 4 = 2.5 \times 10^{18}$$

$$t = 0.065 \text{ sec}$$

See the movie *Men of Honor*.

Question:

A space station has a volume of  $1,000 \text{ m}^3$ . It is filled with 1 atm of  $N_2$  at 298 K. Suddenly a hole with an area of  $1 \text{ cm}^2$  is created by a meteor. What is the pressure in the station after  $10^3$  seconds?  
 $10^4$  seconds?  $10^5$  seconds?  $10^6$  seconds?

Homework Problem: A vacuum chamber has a volume of  $1 \text{ m}^3$  and initially has a perfect vacuum inside. Suddenly a leak develops. The leak turns out to be a pinhole of radius 0.1 mm. The chamber is sitting in a lab at one atm external pressure and 298 K. Assume the lab air is pure nitrogen. How long will it take for the pressure to rise to 1 mTorr inside of the chamber?

Answer: The number of molecules, N, hitting area A in time t is given by  $N = \frac{1}{4} N_A v A t$ ,  
 Where  $N = PV_A / RT$  (at  $10^{-4}$  and 298 K) =  $3.23 \times 10^{18}$ ,  $N_A = PN_A / RT$  (at 1 atm and 298 K) =  $2.46 \times 10^{25} \text{ m}^{-3}$ ,  $v = 475 \text{ m/s}$ ,  $A = 3.1416 \times 10^{-8} \text{ m}^2$ . Solving for t gives  $t = 0.035$  seconds.

## Lecture 5. Real Gases

The ideal gas law,

$$Z = PV/nRT = PV_m/RT = 1,$$

is based on the assumption of non-interacting particles.  
 The quantity  $V_m = V/n$  is the molar volume.

Real atoms and molecules have an intermolecular potential that is responsible for chemical bonds and van der Waals clusters. The long-range potential between neutral

molecules varies as  $-R^{-6}$ . Short range interaction is always repulsive. Example of a chemical bond is  $\text{Na}_2$ :

$R_e=0.308$  nm,  $D_e = 16.6$  kcal/mol,  $D_0=16.4$  kcal/mol.

Extreme case of a weak van der Waals cluster is  $\text{He}_2$ ,

$R_e=0.75$  nm,  $D_e = 0.1$  kcal/mol,  $D_0=2.6 \times 10^{-6}$  kcal/mol.

Result is a non-ideal equation of state,

$$Z = 1 + B'P + C'P^2 + \dots$$

$$Z = 1 + B/V_m + C/V_m^2 + \dots$$

The “virial coefficients,  $B'$ ,  $C'$ , ...  $B$ ,  $C$ ,... can be related to the intermolecular potential.

It is also useful to work with empirical equations of state, just as it is useful to work with empirical potential energy functions. The most famous one is the van der Waals equation of state:

$$P = nRT/(V - nb) - a(n/V)^2$$

$$P = RT/(V_m - b) - a/V_m^2$$

The first term contains a correction for repulsive forces. The second term is caused by attractive forces.

Isotherms are plots of  $P$  vs  $V_m$  for constant  $T$ . See Fig. 1.23.

Ideal gas isotherms are hyperbolas, with  $\frac{\partial P}{\partial V_m} < 0$  always.

The non-ideal isotherm has regions of

$\frac{\partial P}{\partial V_m} > 0$ , which correspond to a phase transition.

At low temperatures the isotherm has a minimum and a maximum. As  $T$  increases, the min and max get closer and finally merge at a point of inflection, called the critical point.

This point is defined by the conditions  $\left(\frac{\partial P}{\partial V_m}\right)_T = 0$  and  $\left(\frac{\partial^2 P}{\partial V_m^2}\right)_T = 0$ .

Solving these equations for the van der Waals equation gives

$$\begin{aligned} V_{m,c} &= 3b \\ RT_c &= 8a/27b \\ P_c &= a/27b^3 \end{aligned}$$

Define the dimensionless (reduced) variables:

$$\begin{aligned}P_r &= P/P_c \\V_r &= V_{m,c}/V_c \\T_r &= T/T_c\end{aligned}$$

Substituting back into the van der Waals equation gives a universal curve:

$$P_r = 8T_r/(3V_r - 1) - 3/V_r^2.$$

The fact that it is universal is called the law of corresponding states. This implies only that the real equation of state can be well described by just two parameters.

We also find that

$$Z_c = P_c V_c / RT_c = 3/8.$$

Expanding the van der Waals equation of state as a virial series:

$$\begin{aligned}P &= RT/(V_m - b) - a/V_m^2 \\Z = PV_m/RT &= V_m/(V_m - b) - a/(RTV_m) \\&= 1/(1 - b/V_m) - a/(RTV_m) + \dots \\&\cong 1 + b/V_m - a/(RTV_m) + b^2/V_m^2 \\Z &= 1 + \frac{b - a/RT}{V_m} + \frac{b^2}{V_m^2} + \dots\end{aligned}$$

## Lecture 6: The First Law

1. The internal energy of an isolated system is constant. This is equivalent to the statement that  $U$  is a state variable.

Because  $U$  is a state variable, the change in  $U$  caused by a change of state does not depend on the path.

We define  $w > 0$  as the work done on the system. It follows that  $w < 0$  corresponds to work by the system on its surroundings. Similarly,  $q > 0$  is for an endothermic process and  $q < 0$  is for an exothermic process. If we consider  $w$  and  $q$  as the only sources of energy change, then

$$\Delta U = U_f - U_i = w + q$$

regardless of the path-dependent values of  $w$  and  $q$  individually.

Types of paths:

- Insulating walls  $\Rightarrow q=0$

This is called an adiabatic path, and the work done is adiabatic work,  $w_{ad}$ .

$$w=w_{ad}$$
$$\Delta U=w_{ad}$$

- No work done:  $w=0$

$$\Delta U=q$$

- General case:  $\Delta U= w + q$

**Important concept:** We are free to choose any path we wish connecting a given initial and final state in order to calculate  $\Delta U$ . In particular, we may choose an adiabatic path in order to **define** energy and heat.

Mechanical definition of energy change:  $\Delta U=w_{ad}$

Mechanical definition of heat:  $q = w_{ad} - w$

Mechanical equivalent of heat:  $w=Jq$

What is the value of  $J$ ? In 1849, Joule came up with a value of 1 cal at  $15^\circ\text{C} = 4.15$  J. The value today is 4.1840.

**Example of the swimming pool:** A pool may be filled either by rain water or by faucet water. Suppose we wish to measure the amount of rain water, but have no direct way of doing so. (It is hard to put a rain gauge on the clouds!) Instead, we use the following strategy. First, we cover the pool with a piece of plastic, and fill the pool with faucet water. We carefully measure the amount of water with a gauge attached to the tap. Next, we drain the pool, remove the sheet, and allow rain water to enter the pool for a period of time. Finally, cover the pool with plastic and fill the rest of the pool with faucet water, again using the gauge on the tap. The difference between two measurements equals to the amount of rain water that fell into the pool.

In this analogy, the plastic sheet is equivalent to the insulating walls, the first gauge measurement is  $w_{ad}$ , the second measurement is  $w$ , and the rain water is  $q$ . The definition of heat is therefore  $w_{ad} - w$ .

2. The work done on an adiabatic system to change its state from a specified initial state to a specified final state is independent of the type of work done.

Other types of paths:

- Isothermal path:  $T_f = T_i$
- Isochoric path:  $V_f = V_i$
- Isobaric path:  $P_f = P_i$
- Cyclic path: Initial and final states are the same,

$$\Delta U = 0$$

3. A system that undergoes cyclic behavior cannot deliver any work without some other change occurring to its surroundings. In other words, a perpetual motion machine “of the first kind” cannot be built. Example: water running down a hill, turning a turbine, and then running back up hill.

One of the most useful concepts is that of a

- reversible path: For such a path, the system is in thermal and mechanical equilibrium throughout.

### Lecture 7: Applications of the First Law

Expansion of a gas:

$$dw = Fdz = -F_{ex}dz = -P_{ex}Adz = -P_{ex}dV$$

Consider the special case of a free expansion (or sudden compression):  $P_{ex}$  is constant.

$$w = - \int_{V_i}^{V_f} P_{ex} dV = -P_{ex} (V_f - V_i) = -P_{ex} \Delta V$$

We cannot say anything about  $\Delta U$  for this process unless additional information is given (i.e., unless additional constraints are imposed).

Suppose  $V=V_f$  is fixed. Then  $P_f V_f = nRT_f$ , but  $P_f$  and  $T_f$  are not determined. We have insufficient information to calculate  $q$  and  $\Delta U$ .

Suppose  $P_f=P_{ex}$  is fixed. Then  $P_f V_f = nRT_f$ , but  $V_f$  and  $T_f$  are not determined.

What type of additional information do we need?

1) If the process is isothermal,  $T_f = T_i$ . Then knowing either  $P_f$  or  $V_f$  is sufficient to determine the final state.

2) If the process is adiabatic,  $q=0$ ,  $\Delta U = w$ , and  $U_f = U_i + w$ .

## Isothermal Processes

$$T_i, V_i, P_i \Rightarrow T_f, V_f, P_f$$

$$T_i = T_f$$

1) Sudden isothermal expansion:  $P_{\text{ex}} = P_f < P_i$

$$w = - \int_{V_i}^{V_f} P_{\text{ex}} dV = -P_f \int_{V_i}^{V_f} dV = -P_f (V_f - V_i)$$

But  $P_i V_i = P_f V_f$  or  $V_f = P_i V_i / P_f$

$$w = -V_i (P_i - P_f)$$

$$q = V_i (P_i - P_f)$$

Numerical example:

$$P_i = 2 \text{ atm}, P_f = 1 \text{ atm}, V_i = 0.1 \text{ liter}$$

$$w = -0.1 \text{ liter atm} = -0.1 [10^{-3} \text{ m}^3 \times 101,325 \text{ pa}] \\ = -10.13 \text{ J}$$

2) Reversible isothermal expansion

$$w = - \int_{V_i}^{V_f} P dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i} = -P_i V_i \ln \frac{P_i}{P_f} \\ = -0.2 \ln 2 \text{ liter atm} = -14.04 \text{ J}$$

Look at the indicator diagrams.

**Conclusion: More work is extracted in the reversible process.**

3) Sudden compression:  $P_{\text{ex}} = P_f > P_i$

Numerical example:

$$P_i = 1 \text{ atm}, P_f = 2 \text{ atm}, V_i = 0.2 \text{ liter}$$

$$w = 0.2 \text{ liter atm} = 20.27 \text{ J}$$

4) Reversible compression:

$$w = -0.2 \ln 2 \text{ liter atm} = -14.04 \text{ J}$$

Look at the indicator diagrams.

Conclusion: More work is required in the irreversible process.

Claim: Reversible isothermal expansions always deliver more work than irreversible ones.

That is,  $-w_{\text{rev}} > -w_{\text{irr}}$   
 where  $w_{\text{rev}} = -nRT \ln(V_f/V_i)$   
 and  $w_{\text{irr}} = -P_f(V_f - V_i)$

Proof: In both cases,  $V_f = nRT/P_f$

Claim:  $V_f - V_i < V_f \ln(V_f/V_i) = -V_f \ln(V_i/V_f)$

That is,  $1 - V_i/V_f < -\ln(V_i/V_f)$

Define:  $x = 1 - V_i/V_f$

Claim:  $x < \ln(1-x)$  for  $0 < x < 1$

This is equivalent to  $x < x + x^2/2 + x^3/3 + \dots$

QED

## Lecture 8. Energy and Heat Capacity

How does the energy vary with temperature?

$$U = U(T, V)$$

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

For an ideal gas:

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT = C_V(T) dT$$

The change in energy along any path is

$$\Delta U = \int_{T_i}^{T_f} C_V(T) dT$$

$C_V$  is the heat capacity at constant volume.

$$U = U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}} + U_{\text{elec}}$$

For **any atom or molecule**:  $U_{\text{trans}} = (3/2)nRT$   
(3 degrees of freedom)

For a **linear molecule**:  $U_{\text{rot}} = nRT$  (2 d. f.)

For a **non-linear molecule**:  $U_{\text{rot}} = 3/2nRT$  (3 d. f.)

For a **diatomic molecule**:  $U_{\text{vib}} = \frac{nN_A h\nu}{\exp(h\nu/kT) - 1}$

This result is derived by setting  $E_v = v h\nu$ ,  
 $P(E_v) = C \exp(-E_v/kT)$ , and summing over  $v$ .

For a **polyatomic molecule**, take the sum over all vibrations.

In most cases,  $U_{\text{elec}}$  is nearly zero.

$$C_{v,\text{trans}} = 3/2 nR$$

$$C_{v,\text{rot}} = nR \text{ or } 3/2 nR$$

$$C_{v,\text{vib}} = nRf^2 \text{ where } f = \frac{h\nu}{kT} \frac{\exp(-h\nu/2kT)}{(1 - \exp(-h\nu/kT))}$$

Derive the last result. Show that at low  $T$ ,  $f=0$ , and at high  $T$ ,  $f=1$ .)  
This can be done by expanding the denominator:

$$1 - \exp(-h\nu/kT) \approx 1 - (1 - h\nu/kT) = h\nu/kT$$

These results are all examples of the equipartition theorem.

$C_V$  is an extensive quantity, with units  $J K^{-1}$ . It is practical to define the intensive equivalents:

$$\text{Molar heat capacity: } C_{v,m} = C_V/n \text{ (} J K^{-1} \text{ mol}^{-1}\text{)}$$

$$\text{Specific heat capacity: } C_{v,m}/M \text{ (} J K^{-1} \text{ g}^{-1}\text{)}$$

Physical meaning of the heat capacity:

•The difference in energy between any two states is given by  $\Delta U = \int_{T_i}^{T_f} C_V dT$ .

This result assumes ideal behavior.

It is also true that

$$dU = dw + dq = -PdV + dq$$

But at constant volume,  $dw=0$ .

Therefore, after integration,

$$\Delta U = q_v$$

where  $q_v$  is the heat absorbed at constant volume.

Example:

State 1:  $n=1$  mole,  $P_1= 1$  atm,  $T_1=300$  K,  $V_1=24.62$  l

State 2:  $P_2=P_1$ ,  $T_2=2T_1$ ,  $V_2=2V_1$

State 3:  $P_3=(1/2)P_1$ ,  $T_3=T_1$ ,  $V_3=2V_1$

Path A:  $1 \rightarrow 2$  at constant pressure

Path B:  $2 \rightarrow 3$  at constant volume

Path C:  $3 \rightarrow 1$  at constant temperature

Calculate  $w$ ,  $q$ , and  $\Delta U$  along each reversible path and for the entire cycle. Assume the gas consists of atoms.

$$\Delta U = (3/2)nR\Delta T = 12.47 \Delta T \text{ Joules}$$

$$\Delta U_A = 3.74 \text{ kJ}$$

$$\Delta U_B = -3.74 \text{ kJ}$$

$$\Delta U_C = 0$$

$$w_A = -P_1 \Delta V = -24.62 \text{ liter atm} = -2.495 \text{ kJ}$$

$$w_B = 0$$

$$w_C = -nRT \ln(V_2/V_1) = 1.729 \text{ kJ}$$

$$w_{\text{cycle}} = -0.766 \text{ kJ}$$

$q = \Delta U - w$  for each step.

## Lecture 9: Enthalpy and Heat Capacity

Suppose the heat is **not** supplied at constant volume. Typically experiments are performed in the open air, *i.e.*, at constant pressure. But in that case, the system must also undergo PV work, and more heat is required to get the same increase in T. This heat is called the **enthalpy, H**.

Definition:  $H = U + PV$

Clearly, H is a state variable. What other properties does it have?

$$\begin{aligned}dH &= dU + PdV + VdP \\&= dq + dw + PdV + VdP \\&= dq + VdP\end{aligned}$$

At constant pressure,  $dP = 0$  and

$$dH = dq_p$$

$$\Delta H = q_p$$

For an **ideal gas**,  $PV = nRT \Rightarrow H = U + nRT$

For constant n,  $\Delta H = \Delta U + nR\Delta T$

For constant T,  $\Delta H = \Delta U + RT\Delta n$

For constant n and T,  $\Delta H = \Delta U$

Note:  $\Delta H$  is not equal to  $\Delta U + P\Delta V + V\Delta P$ .

Heat capacity at constant pressure:

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

How are  $C_p$  and  $C_v$  related?

For an ideal gas:  $H = U + nRT$

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P = \left( \frac{\partial U}{\partial T} \right)_P + nR$$

$$C_P = C_V + nR, \quad C_{P,m} = C_{V,m} + R$$

Empirical result:  $C_{P,m} = a + bT + c/T^2$

$$\Delta H = a(T_2 - T_1) + \frac{1}{2} b(T_2^2 - T_1^2) - c(T_2^{-1} - T_1^{-1})$$

Example: Heating of  $I_2$  at constant pressure

Phase	a	b	c
solid	40.12	0.04979	0
liquid	80.33	0	0
vapor	37.40	0.00059	-0.71e+5

Melting point = 386.8 K

Boiling point = 458.4 K

Enthalpy of fusion = 15.52 kJ/mol

Enthalpy of vaporization = 41.80 kJ/mol

Calculate the heat necessary to raise one mole of  $I_2$  from  $T_1$  to  $T_2$  at 1 atm.

a)  $T_1 = 100 \text{ K}, T_2 = 200 \text{ K}$

$$q_P = 40.12 (200 - 100) + \frac{1}{2} \times 0.04979 (200^2 - 100^2) = 4.76 \text{ kJ}$$

b)  $T_1 = 100 \text{ K}, T_2 = 400 \text{ K}$

$$q_P = 40.12 (386.8 - 100) + \frac{1}{2} \times 0.04979 (386.8^2 - 100^2) + 15,520 + 80.33(400 - 386.8) = 31.56 \text{ kJ}$$

c)  $T_1 = 100 \text{ K}, T_2 = 500 \text{ K}$

$$\begin{aligned} q_P &= 40.12 (386.8 - 100) + \frac{1}{2} \times 0.04979 (386.8^2 - 100^2) + 15,520 + \\ &80.33(458.4 - 386.8) + 41,800 \\ &+ 37.40(500 - 458.4) + \frac{1}{2} \times 0.00059(500^2 - 458.4^2) \\ &- 0.71 \times 10^5 (500^{-1} - 458.4^{-1}) = 79.63 \text{ kJ} \end{aligned}$$

## Lecture 10. Adiabatic Processes

General case:  $q_{ad} = 0, \Delta U_{ad} = w_{ad}$

Irreversible adiabatic expansion:  $w_{\text{ad,irr}} = -P_f(V_f - V_i)$

Reversible adiabatic expansion:

What shape does a reversible adiabat have in a P-V diagram? (Recall that an isotherm is a hyperbola.)

We have two equally valid descriptions of the energy change:

$$dU = C_V dT \text{ (ideal gas)}$$

$$dU = -PdV \text{ (for a reversible adiabat)}$$

$$\therefore C_V dT = -PdV = -nRT dV/V \text{ (ideal gas)}$$

$$\therefore C_V dT/T = -nR dV/V$$

If we assume that  $C_V$  is constant, then integration gives

$$\ln(T_f/T_i) = -(nR/C_V) \ln(V_f/V_i) = (nR/C_V) \ln(V_i/V_f)$$

$$\frac{T_f}{T_i} = \frac{P_f V_f}{P_i V_i} = \left( \frac{V_i}{V_f} \right)^{nR/C_V}$$

$$\frac{P_f}{P_i} = \left( \frac{V_i}{V_f} \right)^{1+nR/C_V}$$

$$1 + nR/C_V = (C_V + nR)/C_V = C_p/C_V \equiv \gamma$$

$$\therefore P_i V_i^\gamma = P_f V_f^\gamma$$

Equivalent result:  $\frac{T_f}{T_i} = \left( \frac{P_f}{P_i} \right)^{\frac{\gamma-1}{\gamma}}$

(Prove this by replacing  $V$  with  $nRT/P$  on both sides.)

Value of  $\gamma$  for an ideal gas:

Atoms:  $\gamma = 5/3$

Rigid rotor:  $\gamma = 7/5$

Diatomic molecule with vibration fully active:

$$\gamma = 9/7$$

### Comparison of reversible and irreversible adiabatic expansion of an ideal gas:

Irrversible case:  $\Delta U_{ad,irr} = w_{ad,irr} = -P_f(V_f - V_i)$

(same form as the irreversible isothermal expansion)

$$w_{ad,irr} (=w_{ad,rev}) = C_v(T_f - T_i)$$

Equating these results gives

$$P_f V_f - P_f V_i = C_v T_i - C_v T_f$$

$$nRT_f - P_f V_i = C_v T_i - C_v T_f$$

$$(nR + C_v)T_f = C_v T_i + P_f V_i$$

$$T_f = (C_v T_i + P_f V_i)/C_p = T_i/\gamma + P_f V_i/C_p$$

$$= T_i/\gamma + (P_f/P_i)P_i V_i/C_p = T_i/\gamma + (P_f/P_i)nRT_i/C_p$$

$$= T_i/\gamma + (P_f/P_i)[(C_p - C_v)/C_p]T_i$$

$$= T_i/\gamma + (P_f/P_i)[1 - 1/\gamma]T_i$$

$$= T_i [1/\gamma + (\gamma-1)/\gamma (P_f/P_i)]$$

Reversible case:  $T_f = T_i \left( \frac{P_f}{P_i} \right)^{\frac{\gamma}{\gamma-1}}$

Claim that more work is done reversibly. That is,

$$\left( \frac{T_f}{T_i} \right)_{rev} < \left( \frac{T_f}{T_i} \right)_{irrev}$$

$$\left( \frac{P_f}{P_i} \right)^{\frac{\gamma-1}{\gamma}} < \frac{1}{\gamma} + \left(1 - \frac{1}{\gamma}\right) \frac{P_f}{P_i}$$

Define:  $x = P_f/P_i < 1$  and  $a = (\gamma-1)/\gamma < 1$ .

Want to show that  $x^a - ax < 1 - a$

Define  $f(x) = x^a - ax$ .

Clearly,  $f(0) = 0$  and  $f(1) = 1 - a$

∴ All we need to show is that  $f(x)$  increases monotonically with  $x$ . This is equivalent to showing that  $df/dx > 0$  for  $0 < x < 1$ .

$$df/dx = ax^{a-1} - a = a(x^{-(1-a)} - 1) > 0$$

because  $x < 1$  and  $a < 1$ .

QED

Famous application: a cycle consisting of two isotherms and two adiabats.

We will use the notation of figure 4.5.

State A:  $T_{\text{hot}}, V_A$

State B:  $T_{\text{hot}}, V_B$

State C:  $T_{\text{cold}}, V_C$

State D:  $T_{\text{cold}}, V_D$

Path 1: Isotherm,  $T = T_{\text{hot}}$

Path 2: Adiat,  $T_{\text{hot}} \rightarrow T_{\text{cold}}$

Path 3: Isotherm,  $T = T_{\text{cold}}$

Path 4: Adiat,  $T_{\text{cold}} \rightarrow T_{\text{hot}}$

$$w_1 = -nRT_{\text{hot}} \ln(V_B/V_A) \quad q_1 = nRT_{\text{hot}} \ln(V_B/V_A)$$

$$w_2 = C_V(T_{\text{cold}} - T_{\text{hot}}) \quad q_2 = 0$$

$$w_3 = -nRT_{\text{cold}} \ln(V_D/V_C) \quad q_3 = nRT_{\text{cold}} \ln(V_D/V_C)$$

$$w_4 = -C_V(T_{\text{cold}} - T_{\text{hot}}) \quad q_4 = 0$$

Show that  $V_A/V_B = V_C/V_D$

$$w_{\text{tot}} = -nR(T_{\text{hot}} - T_{\text{cold}}) \ln(V_B/V_A) = -q_{\text{tot}}$$

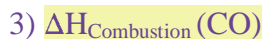
## Lecture 11: Thermochemistry

Central concept:  $\Delta H_{\text{cycle}} = 0$

Example 1: Enthalpy of combustion of CO at 298 K



Set up a cycle to illustrate the concept:



At 298 K and 1 atm,

$$\Delta H_f(\text{CO}) = -110.53 \text{ kJ/mol}$$

$$\Delta H_f(\text{CO}_2) = -393.51 \text{ kJ/mol}$$

$$\Delta H_f(\text{O}_2) = 0$$

$$\Delta H(\text{path 1}) + \Delta H(\text{path 2}) = \Delta H(\text{path 3})$$

or

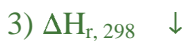
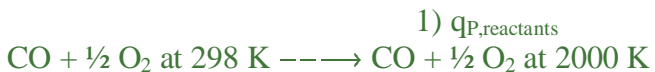
$$\Delta H(\text{path 2}) = \Delta H(\text{path 3}) - \Delta H(\text{path 1})$$

or

$$\Delta H_{\text{reaction}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$

$$\Delta H_{\text{combustion}} = -393.51 - (-110.53) = -282.98 \text{ kJ/mol}$$

Example 2: Enthalpy of combustion of CO at 2000 K



$$\Delta H(\text{path 1}) + \Delta H(\text{path 2}) = \Delta H(\text{path 3}) + \Delta H(\text{path 4})$$

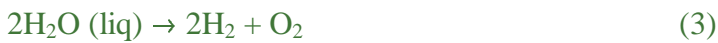
$$q_{P, \text{reactants}} + \Delta H_{r, 2000} = q_{P, \text{products}} + \Delta H_{r, 298}$$

$$\Delta H_{r, 2000} = \Delta H_{r, 298} + (q_{P, products} - q_{P, reactants})$$

$$q_{P, reactants} = \int_{T_i}^{T_2} C_{P, reactants} dT \quad q_{P, products} = \int_{T_i}^{T_2} C_{P, products} dT$$

**Hess' Law:** The standard enthalpy of a reaction equals the sum of the standard enthalpies of individual reactions into which the overall reaction can be divided.

### Example 3: Hydrogenation and Combustion



$$\Delta H_1 = \Delta H_f(C_2H_6) - \Delta H_f(C_2H_2) = 52.26 - 226.73 = -174.47 \text{ kJ/mol}$$

$$\Delta H_2 = 2\Delta H_f(CO_2) + 3\Delta H_f(H_2O, liq) - \Delta H_f(C_2H_6) = 2(-393.51) + 3(-187.78) - 52.26 = -1402.62 \text{ kJ/mol}$$

$$\Delta H_3 = -2\Delta H_f(H_2O, liq) = 375.56 \text{ kJ/mol}$$

$$\Delta H_4 = 2\Delta H_f(CO_2) + \Delta H_f(H_2O, liq) - \Delta H_f(C_2H_2) \\ = 2(-393.51) - 187.78 - 226.73 = -1201.83 \text{ kJ/mol}$$

$$\text{Conclusion: } \Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_4$$

We can demonstrate this result by formally construction a thermodynamic cycle; however, I don't recommend doing this as a problem solving method.



1 ↓

↑ 3



#### Example 4. Bond Enthalpies



↓ 431.8

↑ 338.8



$$4\Delta\text{H}(\text{C-H}) = 431.8 + 471.1 + 421.7 + 338.8 = 1663.4$$

$$\Delta\text{H}(\text{C-H}) = 415.9 \text{ kJ/mol}$$

Subtle point: Bond energies and bond enthalpies are equal only at 0K.