# Chapter 2:: The first law of thermodynamics

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Essentially, the first law states that energy is always conserved.

## Internal energy

In this chapter, we'll define energy as the capacity to supply heat or do work. A system doesn't inherently have heat or work; only if it's transferred. We measure it in the following units::

$$1J = \frac{1 kg m^2}{s^2}$$

$$1 calorie = 4.184 J$$

$$1 calorie_{dietary} = 1000 calories$$

Energy cannot be created or destroyed. Only transferred or converted from one form/object to another.

- **Energy** is the capacity to do work

- In thermodynamics, we are interested in flow of energy in **heat** and **work**. This is because they describe the process of energy transfer.

In essence, for any system $\Omega$,

$$\sum_{\Omega} E = E_{kinetic} + E_{potential}$$

## Forms of energy

- Thermal energy (kinetic and heat)

- Bond energy (potential)

## The first law

Because energy can't be created or destroyed, we can express change in energy in the following ways::

$$\Delta E_\Omega = \Delta E_\sigma + \Delta E_{\sigma^c} = 0$$

$$\implies \Delta E_\sigma = -\Delta E_{\sigma^c}$$

$\forall \Omega$ at rest with no external fields, it can be said that

$$E_\sigma = \Delta U_\Omega = \Delta U_\sigma + \Delta U_{\sigma^c}$$

$U$ (internal energy) is a state function, so

$$\Delta U = U_2 - U_2 = q + w$$

In the simplest processes, only one of $P$, $V$, or $T$ will change at any given time. Some important things to note are the following::

- Isothermal: const temperature, $(\Delta T_\sigma = 0)$

- Isobaric: const pressure, $(\Delta P_\sigma = 0)$

- Isochoric: const volume, $(\Delta V_\sigma = 0)$

- Adiabatic no heat transfer $(q = 0)$

- Cyclic $\implies \Sigma_1 = \Sigma_0$, where $\Sigma_n$ is some arbitrary state or property of a system.

## Internal energy vs heat/work

In a reaction, change in internal energy is expressed as::

$$\Delta U_\Omega = \Delta U_{products} - \Delta U_{reactants}$$

Recall that work is **NOT** a state function!

- When work is positive, $\Delta U_\sigma > 0$ and $\Delta V_\sigma < 0$

- When work is negative, $\Delta U_\sigma < 0$ and $\Delta V_\sigma > 0$

## Expansion work

Let us start by looking at the two pressure inequalities below::

$$P_\sigma > P_{\sigma^c} \implies expansion$$
$$P_\sigma < P_{\sigma^c} \implies compression$$

So we have that

$$P_{\sigma^c} = \frac{F_\sigma}{A}$$
$$dV = Adh$$

Then

$$dw = -F_{\sigma^c}dh = -\frac{F_{\sigma^c}}{A}Adh = -P_{\sigma^c}dV$$

Thus, our final formula for expansion work can be expressed as the following integral::

$$w = -\int_{v_1}^{v_2} P_{\sigma^c}dV$$

where $P_{\sigma^c}$ is a function of the volume of gas in an arbitrary container $\sigma$.
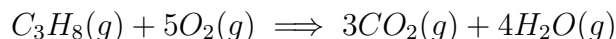
## Why do we care about work?

We care because energy is transferred from the system to the surroundings in the form of work (only applicable to adiabatic systems).

## Work with gases

We can express this idea with the equation:

$$w = -\Delta n RT, \Delta n = v_{prod,(g)} - v_{rxt,(g)}$$

Take the following reaction for example::

$$C_3H_8(g) + 5O_2(g) \implies 3CO_2(g) + 4H_2O(g)$$

Here, we have 6 moles of gas on the reactant side, and 7 on the product side. So we have that $\Delta n = 1$. This means that work was done by the system, thus the sign for work is negative.
In general::

$$\Delta n > 0 \implies w < 0$$
$$\Delta n < 0 \implies w > 0$$

## Example (slide 18)

A greatly simplified model of an internal combustion engine is as follows. At the start of the power stroke the ignited gases exert a pressure of 20 atm, and drive the piston back against a constant force equivalent to 5.0 atm. In so doing, the piston sweeps out 250 cm3. What is the power output of a six-cylinder engine working at 2000 RPM (with one power stroke from each cylinder every second revolution)?

**Solution::** We can start by calculating work.

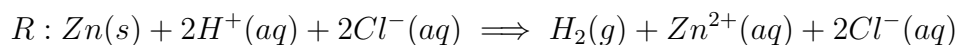$$w = -P\Delta V = -(5atm)(0.25L) = 1.25Latm = 1.25Latm\frac{101.325J}{Latm} = 1.3E2J$$

In six cylinders over a 1 minute duration, we have that,

$$(2000)(6)(w)(0.5) = 7.8E5J$$

Rate of production::

$$P = \frac{w}{t} = \frac{7.8E5}{60s} = 13LW$$

## Example 2 (slide 19)

$$R: Zn(s) + 2H^+(aq) + 2Cl^-(aq) \implies H_2(g) + Zn^{2+}(aq) + 2Cl^-(aq)$$

a) How much work has been done if 5 g of Zn have completely reacted according to the following reaction if the external pressure is 1 atm and T=298K.

$$n(H_2) = n(Zn) = \frac{5g}{65.38\frac{g}{mol}} = 0.0765mol$$

$$\Delta V = \frac{n(H_2)RT}{P} = \frac{0.0765mol(0.08206\frac{Latm}{Kmol})298K}{1atm} = 1.87L$$

b) What's the work per 1 mole of Zn consumed?

$$w = -P\Delta V = \frac{-189J}{0.0765mol} = -2470\frac{J}{mol}$$

## Heat

Recall that heat is not a state function. If $\Delta Q = 0$, the system is at thermal equilibrium. Conservation of energy requires that $q_\sigma + q_{\sigma^c} = 0 \implies q_\sigma = -q_{\sigma^c}$.

## Example 3 (slide 26)

How much heat is transferred in raising the temperature of a beaker of water (50 g) from 25°C to 35°C (at constant P = 1 atm)?

$$q = mc\Delta T = (50g)(4.1840\frac{J}{G^\circ})(10^\circ) = 2092J$$

## Heat capacity

Assume $\sigma$ is closed with no phase changes or reactions.

$$q_\sigma = \int_{T_1}^{T_2} CdT = \int_{T_1}^{T_2} mC^c dt$$

Temperature rising depends on the following::

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1. Amount of heat delivered

2. Amount of substance present

3. Chemical nature and physical state of substance

4. Conditions under which heat is added to substance

Specific heat capacities can be found on **slide 30**. Recall that the higher the heat capacity, the harder it is to add temperature to the substance.

At constant volume::

$$C_V = \frac{\Delta U}{\Delta T} = \frac{q_v}{\Delta T}$$

At constant pressure::

$$C_P = \frac{\Delta H}{\Delta T} = \frac{q_v}{\Delta T}$$

Heat capacity can also be expressed as the limit::

$$\lim_{\Delta T \to 0} \frac{q}{\Delta T}$$

$\Delta U = f(T)$. Internal energy is not a function of volume or pressure. The change in enternal energy can be expressed as the partial differential::

$$\frac{\partial U}{\partial V}_T = 0 \forall g \in \mathbb{C}$$

For sake of simplicity, we'll assume all processes covered in this course are quasi-static.

Internal equilibrium $\equiv$ systems are homogenous.

## Reversible & irreversible processes

**Reversible::** An infinitessimal change **will** change the direction of the process

**Irreversible::** An infinitessimal change **will not** change the direction of the process

In reality, there's no process that's fully reversible. They just progress much slower than irreversible processes.

## PV diagrams (slide 43, 44)

Take a function $V = f(P)$. We want to study the region bound between $P_1$ and $P_2$ as well as $V_1$ and $V_2$. Isothermal curves are hyperbola, because the function is the rational function::

$$PV = nRT \implies P = f(V) = \frac{nRT}{V}$$

Where n and T are constant.

## Example 1

We have 3 moles of an arbitrary ideal gas expanding isothermally ($T = const$). $V_i = 20.0L$, $V_1 = 60.0L$, $T = 27.0°C$. Calculate the work in this process.

## Solution

$$w = -P\Delta V = -(1.0atm)(60 - 20)L = -40Latm = -40Latm(\frac{101.35J}{Latm}) = -4053J = -4.1kJ$$

## Infinitessimal pressure changes for expansion

When this occurs, we need to use integration. Recall that

$$w = -\int_{V_1}^{V_2} P_{ex}dV = -\int_{V_1}^{V_2}(P - dP)dV = -\int_{V_1}^{V_2} PdV$$

Because $P = \frac{nRT}{V} = const$, we have that

$$-nRT\int_{V_1}^{V_2}\frac{1}{V}dV = -nRT(\ln(V_2) - \ln(V_2)) = -nRT(\ln(\frac{V_2}{V_1}))$$

By laws of logarithms.
Thus, we have our derived formula::

$$w = -nRT(\ln(\frac{V_2}{V_1}))\blacksquare$$

**NOTE::** For any real process $\rho \in \mathbb{R}$, $\rho$ is irreversible.

## Summary

- For expansion, $|w_{irreversible}| \geq |w_{reversible}|$

- For compression, $|w_{irreversible}| \leq |w_{reversible}|$

- For irreversible, $w = -P_{ex}\Delta V$

- For reversible, $w = -nRT(\ln(\frac{V_2}{V_1})$

## Example 1 revisited

We have 3 moles of an arbitrary ideal gas expanding isothermally ($T = const$). $V_i = 20.0L$, $V_1 = 60.0L$, $T = 27.0°C$. Calculate the work in this process.

$$w = -nRT(\ln(\frac{V_2}{V_1})) = -(3mol)(8.314\frac{J}{Kmol})(300K)(\ln(\frac{60L}{20L})) = -8.22kJ$$

We get a greater resultant work by assuming the process is reversible.

## First law of thermodynamics summary

Recall that in a temperature dependent system, heat is calculated as::

$$q = \int_{T_1}^{T_2} CdT = \int_{T_1}^{T_2} m\bar{c}dT$$

More formulas on slide 58 and 59.

## Enthalpy revisited

$$H = U + PV$$

$U$, $P$, and $V$ are all state functions $\implies$ $H$ is also a state function. However, we don't care about absolute enthalpy. We care about change in enthalpy. So,

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + P\Delta V + V\Delta P + \Delta P\Delta V$$

Assume $P \equiv const$, we have that,

$$\Delta H = \Delta U + P\Delta V = \Delta U - w = q_p$$

For $g \in \mathbb{C}$,

$$\Delta H = C_P \Delta T$$

For infinitessimal change in $T$,

$$dH = dU + d(nRT) = dU + nRdT$$

Knowing that $dH = C_P dT$ and $dU = C_V dT$, we can substitute into the above equation:
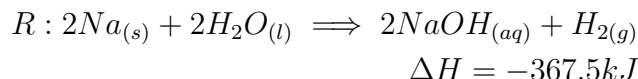
$$C_P dT = C_V dT + nRdT$$
$$C_P = C_V + nR$$
$$C_P - C_V = nR$$
$$\bar{C}_P - \bar{C}_V = R$$

## Difference between $\Delta H$ and $\Delta U$

Consider the following reaction::

$$R : 2Na_{(s)} + 2H_2O_{(l)} \implies 2NaOH_{(aq)} + H_{2(g)}$$
$$\Delta H = -367.5kJ$$

Volume of $H_2$ generated at 1 atm is $24.5L$, so $-P\Delta V = -24.5Latm = -2.5kJ$, $\Delta U = -370kJ$. We can see that $\Delta H \approx \Delta U$

## Example with heat capacity (slide 64)

Calculate $\Delta H$ and $\Delta U$ for the transformation of 1.00 mol of an ideal gas from $27.0°C$ and 1.00 atm to 327°C and 17.0 atm if

$$C_{p,m} = 20.9 + 0.42\frac{T}{K} JK^{-1}mol^{-1}$$

For an ideal gas, $\Delta H$ is given by:

$$\Delta H = \int_{T_1}^{T_2} C_P dT = \int_{T_1}^{T_2} C_{p,m} n dT = \int_{300}^{600} (20.9 + 0.042\frac{T}{K})dT$$
$$= (20.9T + \frac{0.042T^2}{2})|_{300}^{600} = (20.9(600 - 300) + 0.021(600^2 - 300^2))$$
$$\approx 11.9 \times 10^3 J = 11.9kJ$$

## Adiabatic expansion

For adiabatic processes, we always assume that $\Omega \equiv adiabatic \implies q = 0 \forall \Omega$, so,

$$dU = dw = -PdV = -\frac{nRT}{V}dV$$

$$\frac{dU}{nT} = -R\frac{dV}{V}$$

since

$$dU = C_V dt$$

So,

$$\frac{dU}{nt} = \frac{C_V dt}{nT} = \bar{C}_V\frac{dT}{T} = -R\frac{dV}{V}$$

Integrating both sides, we have that

$$\int_{T_1}^{T_2} \bar{C}_V\frac{dT}{T} = -R\int_{T_1}^{T_2} \frac{dV}{V} = \bar{C}_V\ln(\frac{T_2}{T_2}) = R\ln(\frac{V_1}{V_2})$$

Since $\bar{C}_P - \bar{C}_V = R$ for an ideal gas, then.

$$\bar{C}_V\ln(\frac{T_2}{T_1} =)\bar{C}_P - \bar{C}_V\ln(\frac{V_1}{V_2})$$

Divide both sides by $\bar{C}_V$ to obtain::

$$\ln(\frac{T_2}{T_1}) = (\frac{\bar{C}_P}{\bar{C}_V} - 1)\ln(\frac{V_1}{V_2}) = (\gamma - 1)\ln(\frac{V_1}{V_2}) = \ln(\frac{V_1}{V_2})^{\gamma-1}, \gamma = \frac{\bar{C}_P}{\bar{C}_V}$$

$\bar{C}_P$ **and** $\bar{C}_V$ **constants wont be provided on the constant sheet! Review chapter 2 slide 71 for them!**

## Reversible adiabatic expansion $(g \in \mathbb{C})$

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} =$$

We can also do this for $T$ and $P$

$$P_1^{1-\gamma}T_1^{\gamma} = P_2^{1-\gamma}T_2^{\gamma}$$

$$T_1P_1^{\frac{1-\gamma}{\gamma}} = T_2P_2^{\frac{1-\gamma}{\gamma}}$$

## Work done in an adiabatic expansion (slide 74-79)

3.50 moles of an ideal gas are expanded from 450. K and an initial pressure of 5.00 bar to a final pressure of 1.00 bar, and CP,m = 5/2R. Calculate w for the following two cases:

a) The expansion is isothermal and reversible.

b) The expansion is adiabatic and reversible.

$w$ for an isothermal process is given by::

$$w = -nRT(\ln(\frac{V_2}{V_1}))$$

Calculate $V_0$ and $V_f$. Recall that $PV = nRT$ always holds!

$$V_1 = \frac{nRT_1}{V_1} = \frac{(13.5)(0.08314)(450K)}{(5.00)} = 26.2L$$

$$V_2 = \frac{nRT_2}{V_2} = \frac{(3.5)(8.314)(450)}{10^5} = 0.1310m^3$$

$$w = -nRT(\ln(\frac{V_2}{V_1})) = (-3.5)(8.314472)(450K)(\ln(\frac{0.1310}{0.0262})) = -21076J = -21.1kJ$$

For adiabatic:

$$C_V = C_P - R = \frac{5}{2}R - R = \frac{3}{2}R$$

$$T_1P_1^{\frac{1-\gamma}{\gamma}} = T_2P_2^{\frac{1-\gamma}{\gamma}}$$

Now we find $T_2$

$$T_2 = \frac{T_1P_1^{\frac{1-\gamma}{\gamma}}\gamma}{P_2^{\frac{1-\gamma}{\gamma}}}$$

After some plugging in, we get $T_2 = 236K$. Now we can calculate work!

$$w = C_V(T_2 - T_1) = \frac{3}{2}(8.314)(3.5)(236 - 450) = -9.23kJ$$

In general, gases with the same parameters will have the following property::

$$|w|_{isothermal(exp)} > |w|_{adiabatic(exp)}$$

## Irreversible adiabatic expansions

Assume $P_2 = P_{ext}$ and $q = 0$ by definition of adiabatic.

$$\Delta U = w$$

$$n\bar{C}_V(T_2 - T_1) = -P_2(V_2 - V_1)$$

But,

$$V_1 = \frac{nRT_1}{P_1}, V_2 = \frac{nRT_2}{P_2}$$

So,

$$n\bar{C}_V(T_2 - T_1) = -P_2(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1})$$

## Example

An automobile tire contains air at $320 \times 10^3 Pa$ at $20.0°C$. The stem valve is removed and the air is allowed to expand adiabatically against the constant external pressure of $100 \times 10^3 Pa$ until $P = P_{external}$. For air, $C_{V,m} = \frac{5}{2}R$. Calculate the final temperature. Assume ideal gas behavior.

Since $q = 0$, we have that $\Delta U = w$.

$$C_{V,m}n(T_2 - T_1) = -P_{ext}(V_2 - V_1) = -P_2(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1})$$

We can cancel the $n$ values, (full solution on **slide 80**). It's all plugging in. Our final solution would be 0.804.