

### 3.23 Lecture 4

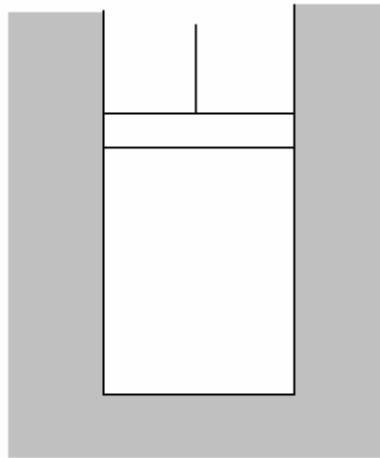
It's easy to look at solutions and understand, but the question is whether I would have gotten the solution. The hard part is making an abstraction and turning it into math. Solutions can be 3 - 4 lines. There are many different solutions.

Today we review ideal gases. Thermodynamics is applied to ideal gases.

#### **Expansion in tire**

Consider the reversible adiabatic expansion of air in a tire. There is expansion across the valve. The pressure is higher outside. It is an irreversible expansion.

The constraint imposed is that the expansion is adiabatic. Consider applying work to a gas in an insulated cylinder. The temperature can change, but  $Q = 0$ .



Relate this condition to variables we want to study. From the 1<sup>st</sup> law,  $dU = \delta W + \delta Q$

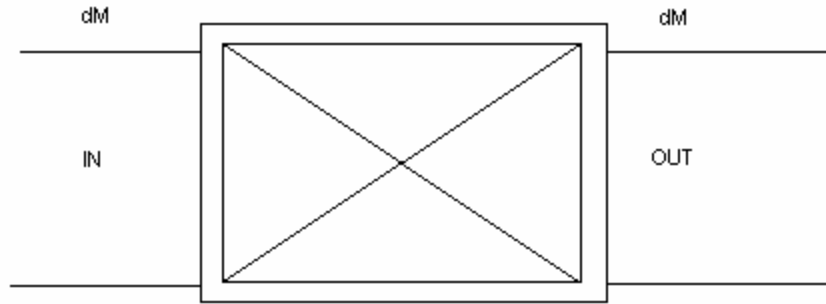
$$nC_V dT = -pdV$$

The differential equation explains the process. Do mathematical manipulations to obtain the expression below

$$(T_2 / T_1)^{C_p/R} = P_2 / P_1$$

#### **Expansion across the valve (Joule-Thompson expansion)**

A problem with the expansion across the valve is that the path is not described. The differential is path dependent.



The possibility of turbulence and other factors means that the integration is not permissible.

A strategy when there are changes of state that can't be tracked is to move up a level. Look at work and heat flows at a higher level. Move boundaries up and look at flow across larger boundaries.

Take the valve as a whole as the system. It is known what happens to the valve. Stuff comes in at a pressure and leaves at a certain pressure. The valve is neither giving or receiving work. Stuff is flowing in and out. Work is being delivered across the boundary. There is a pressure pushing the gas in. This is flow work. There are mass terms in flow work. The valve gains and loses energy associated with stuff coming in and out.

Is there a heat flow? There is a temperature gradient but we need more data. Assume that there is no heat flow. The temperature of the air in the tire is changing, so there would be heat flow. Solve the limiting case where there is no heat flow.

$$\Delta U_{valve} = \delta W + \delta Q + U_{in}\delta_{in} - U_{out}\delta_{out} + P_{in}V_{in}\delta M - P_{out}V_{out}\delta M$$

The terms  $U_{in}\delta_{in}$  and  $U_{out}\delta_{out}$  are related to the flow of gas in and out. Assume that the same amount of gas flows in and out. There is work pushing the gas in and out.

The last two terms are related to enthalpy. The input volume is displaced, and there is a pressure by which it is moved.

At steady state,  $\Delta U_{valve} = 0$ . At any time there is the same energy. This allows us to relate the energy of the system entering and leaving. All properties of the valve are removed and the temperatures are related.

$$\begin{aligned} U_{in} + P_{in}V_{in} &= U_{out} + P_{out}V_{out} \\ U_{in} - U_{out} &= P_{in}V_{in} - P_{out}V_{out} \\ \Delta U &= RT_{in} - RT_{out} \\ C_V\Delta T &= -R\Delta T \\ \Delta T &= 0 \end{aligned}$$

There are two expansions: the adiabatic expansion in the tire and the expansion across the valve. In the tire, the expanding gas loses energy and the temperature lowers. In the case of valve, there is no loss of energy and no  $\Delta T$ .

In an adiabatic reversible process, work is released to the environment and there is no change in entropy. In an adiabatic irreversible process, some energy leaves the system, and there is a change in entropy.

The change in entropy is not zero. The change in internal energy is zero and the temperature is zero.

Why is the valve process irreversible? There is no way of giving off work to the environment. When a volume element is enclosed by a balloon, work can be released to the environment. In a valve, the volume can't be displaced. The work done by the expanding gas stays in the valve

Plug in the following values to find temperature  $T_2$ .

$$\begin{aligned} T_1 &= 300\text{K} \\ P_1 &= 345 \text{ atm} \\ T_2 &= 300 ( 1 / 4.45 )^{8.314 / 33} = 206 \text{ K} \\ T_2 &= - 67^\circ \text{ C} \end{aligned}$$

The temperature is not nearly this cold. There are irreversibilities, such as heat being picked up from the valve.

Consider an enormous mass of gas expanding. There is nothing next to it to give off heat. Wet air, saturated with moisture, rises at it goes over the mountain. As it expands, there is nothing to give heat off to. The temperature drops and rain falls out. As the air crosses into Eastern Washington, the air compresses again. Eastern Washington is a desert. This is an explanation why Utah and Nevada are so dry. All the moisture left. When two saturated air masses with different temperature mix, there is always rain. This is why the world survives.



## Enthalpy

This is introduced for convenience. This is a derivative property of materials. There is energy in bringing matter into a system. There is energy associated with flowing mass.

$$H = U + PV$$

Calculate heat flows under constant pressure. Look at  $Q$  under constant  $P$ .

$$dU = \delta Q + \delta W$$

$$dU = \delta Q - pdV$$

$$\delta Q = dU + pdV$$

Enthalpy is a state function.

$$H = U + PV$$

$$dH = dU + pdV + VdP$$

$$dU = \delta Q - pdV$$

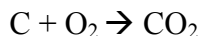
$$dH = \delta Q + pdV$$

$$(dH)_P = (\delta Q)_P$$

The condition of constant pressure makes  $dH$  exact. The change of enthalpy at constant pressure is equal to heat flow. It is important to know the assumptions. An assumption is that there is only  $pdV$  work with not other terms and there is constant pressure. The equations are not true if these assumptions are not true. Enthalpy is used frequently and is tabulated.

For elements in their steady state at 298 K and  $P = 1$  atm,  $H = 0$ . This is just convention. In compounds, the energy is given by the formation enthalpy from elements at 298 K, 1 atm.

Measure heat flow at 298 K, 1 atm. This would help get  $\Delta H$  formation of  $\text{CO}_2$ . When finding values, only the end pressure and beginning pressure need to be the same.



There is an enormous number of sources of data (google, Kubaschewskit, NIST.gov)

## Integrating enthalpy

Enthalpy varies with temperature, and the function  $H(T)$  needs to be integrated with temperature.

$$(dH)_P = (\delta Q)_P$$

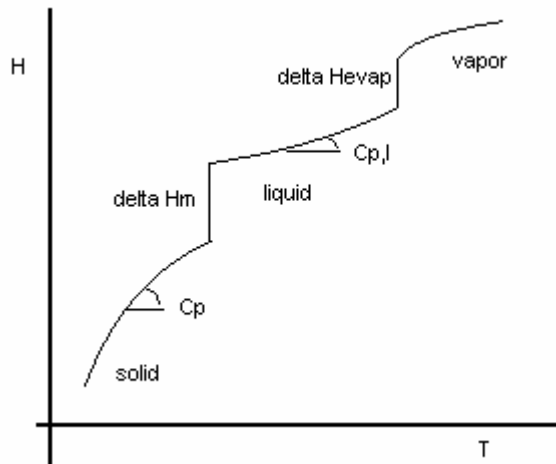
$$(dH)_P = nC_P(dT)_P$$

Divide by  $(dT)_P$  to get the partial differential.

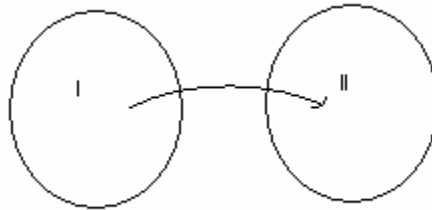
$$(dH / dT)_P = C_P$$

The slope is the heat capacity.

### Graph of Enthalpy



### Enthalpy of phase transitions



$$H = U + PV$$
$$\Delta H = \Delta U - \Delta PV$$

Heat has to be put in to do phase transformations. There are two sources of energy flows. A lot of energy is absorbed in bond breaking. The internal energy term is  $\Delta U$ . An extra term in macroscopic thermodynamics is  $p\Delta V$ . Boundaries of the system are displaced.

### Estimate $p\Delta V$

Imagine a solid to solid transformation. The molar volume is  $V$ , and a good estimate per mole for metals is 10 cc. What is a reasonable value of  $\Delta V$ ? Solids don't change dramatically. One cubic centimeter per mole is a good estimate

$$p\Delta V = 10^5 \text{ Pa (1 atm)} 10^{-6} \text{ m}^3 / \text{mol}$$

$$p\Delta V = 0.1 \text{ J / mol}$$

The change in internal energy is on the scale of  $kJ$ . Bonds are on the scale of  $kJ$ . When does  $p\Delta V$  become large? Geologists study systems with large  $P$ . The term  $p\Delta V$  matters in the transition from liquid to vapor. The change in volume is very large.

### Heats of phase transformation

Below are empirical rules that work for metals

$$\Delta H_m (J) = 9 T_m(K) \quad \text{Richard's rule}$$

$$\Delta H_{evap} (J) = 90 T_{evap}(K) \quad \text{Trouton's rule}$$

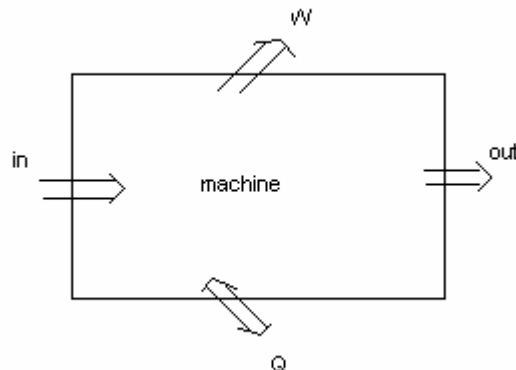
The expressions are in terms of J / mol. The difference of magnitude between Richard's rule and Trouton's rule is a statement of entropy. The entropy ( $\Delta H_m / T$ ) is rather constant across the periodic table. Below are typical values of energy associated with transitions.

1 $kJ$	solid-solid
10 $kJ$	melting
100's $kJ$	evaporation

With stronger bonding, such as in the case of  $ZrO_2$ , the magnitude of the enthalpy of phase transformation is higher. Enthalpy is useful in calculations of heat and is associated with flowing matter. This is practical in mechanical engineering

### Machine

Below is a schematic of a machine



Below is a description of the energy flow in a machine. The change in internal energy for the machine is zero at steady state.

$$\Delta U_{machine} = Q + W + H_{in} - H_{out}$$

$$Q + W = H_{out} - H_{in}$$

This last expression is used in almost anything. In mechanical engineering, this is used to describe the energy flow in a refrigerator.

### Change of state of a material in terms of thermodynamic equations

Look at the changes of state of a material in terms of the thermodynamic equations. Below is an expression relating the input of heat to the change of enthalpy associated with evaporating water at constant pressure.

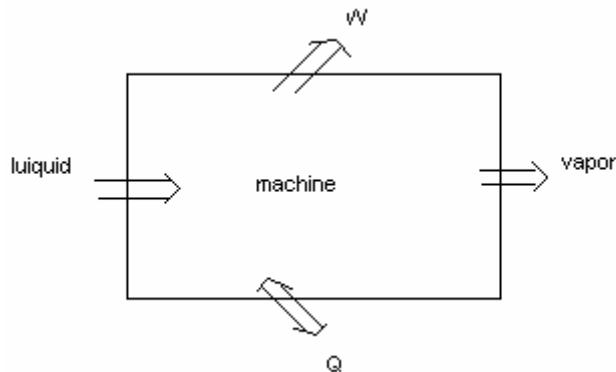
$$Q = H_{final} - H_{initial}$$

$$Q = \Delta H_{evaporation}$$

The term  $H_{final}$  is associated with the final state (vapor) and the term  $H_{initial}$  is associated with the initial state (liquid)

### Change of state of a material in terms of a process

Look at evaporation as a process. Below is a picture of an evaporator.



The equation relating work and heat flow to change in enthalpy is

$$Q + W = H_{out} - H_{in}$$

The work term is zero

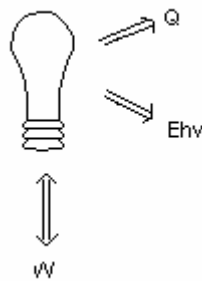
$$Q = H_{vapor} - H_{liquid}$$

There are a variety of types of problems involving simple enthalpy calculations, heat capacity, and reaction enthalpy. The definition of boundaries involve some level of abstraction.

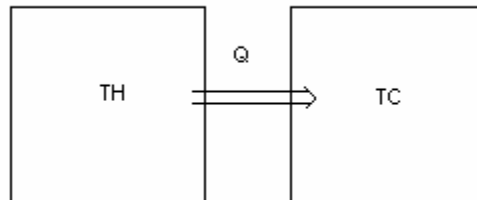
## 2<sup>nd</sup> law of thermodynamics

This is a very pragmatic law. It involves the conversion of heat to work. It was developed in the pumping of water out of mines. It's a pragmatic law because we know how to burn.

In the case of the light bulb, is there more heat or light created? Ninety percent of the work goes to heat. The system must conserve energy. The reverse process is allowed but does not happen.



Consider the transfer of heat from a hot body to a cool body.

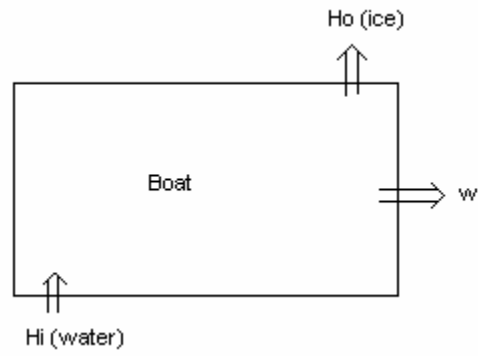
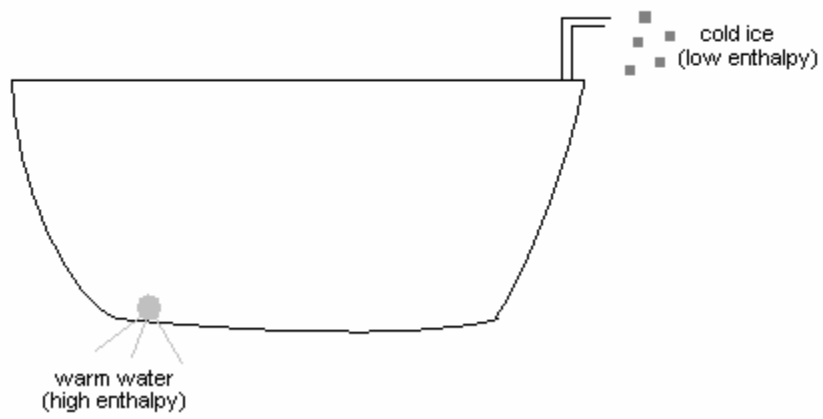


$$\begin{aligned}Q_H &= -Q_C \\Q_H + Q_C &= 0 \\-(Q_H) + (-Q_C) &= 0\end{aligned}$$

The first law is satisfied if the heat flow were to flow in the other direction. The total energy is conserved.

Consider a party boat.





This boat satisfies the first law but not the second law