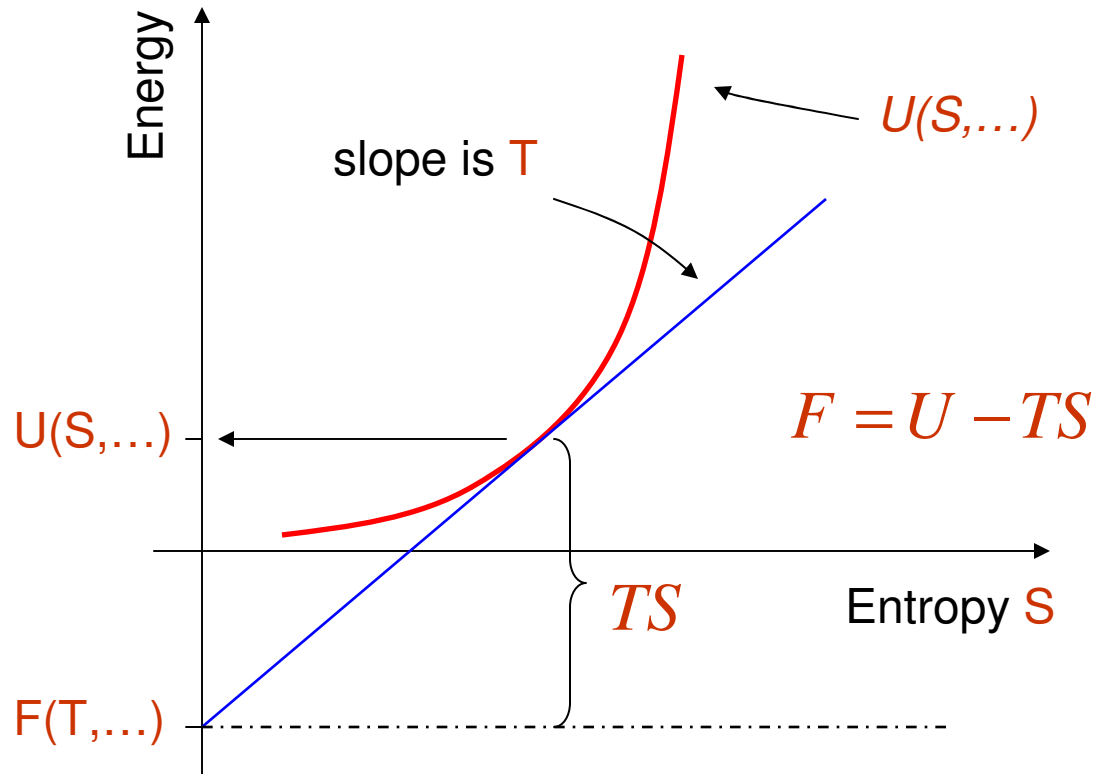


## Some properties of the Helmholtz free energy



From the properties of  $U$  vs  $S$ , it is clear that the Helmholtz free energy is always algebraically less than the internal energy  $U$ .

Since  $F$  characterizes the work that can be extracted from the system, the relation  $F < U$  tells us that not all internal energy can be converted into work.

## *Helmholtz potential - link to statistical physics*

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Link to statistical physics:

$$F(T, V, N) = -k_B T \ln(Z)$$

Where  $Z$  is the partition function:

$$Z(T, V, N) = \sum_j \exp\left(-\frac{E_j(V, N)}{k_B T}\right)$$

$F$  is easy to calculate in statistical physics if you know the energy spectrum  $E_j$  of the system of interest.

## *The Helmholtz free energy and the Euler equation*

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From the fact that energy is a homogeneous function of the extensive parameters, we have derived the Euler equation:

$$U = TS - PV + \mu N + \dots$$

When we apply the Legendre transformation to  $U$  in the form of the Euler equation, we obtain the Euler equation for the Helmholtz free energy:

$$F = U - TS = -PV + \mu N + \dots$$

## *The Helmholtz free energy and the Euler equation*

---

We can also write the Helmholtz free energy in its differential form:

$$dU = TdS - PdV + \mu dN + \dots$$

$$dF = dU - TdS - SdT$$

$$dF = -SdT - PdV + \mu dN + \dots$$

# The Enthalpy

---

Legendre transformation to obtain enthalpy:

$$H(S, P, N, \dots) = U + PV$$

Enthalpy should be used for calculation of the equilibrium state if pressure is maintained constant (the system of interest **in contact with a pressure reservoir**).

# The Enthalpy

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Differential of enthalpy:

$$dH = TdS + VdP + \mu dN + \dots$$

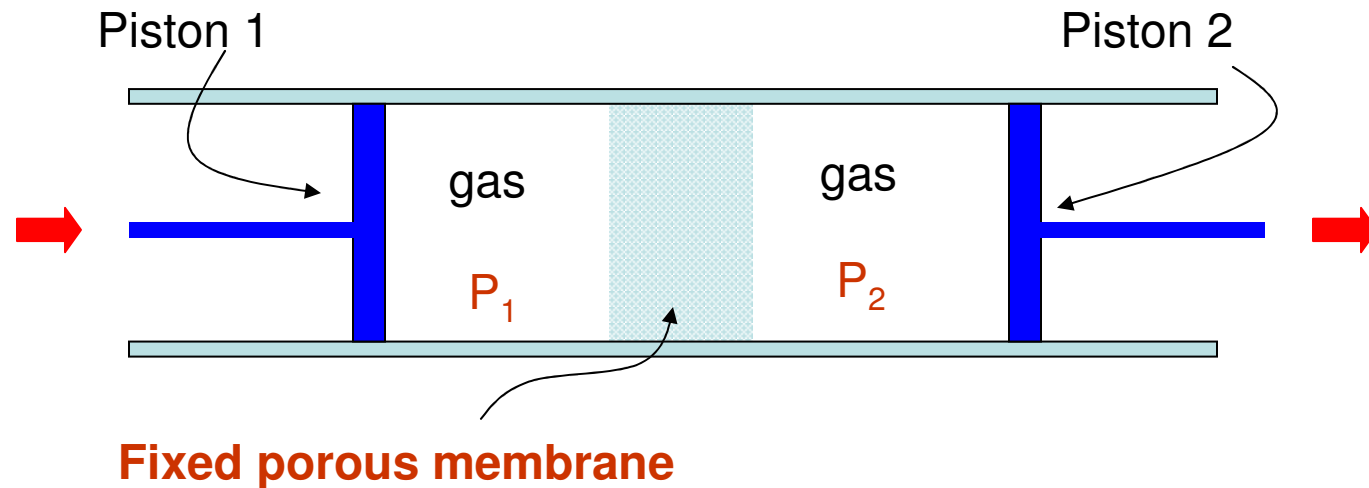
If the pressure is constant and the number of particles in the system does not change then  $dP = 0$  and  $dN = 0$ :

$$dH = TdS = \delta Q$$

Therefore, heat added to the system at constant pressure is equal to the increase of enthalpy.

## The Joule-Thomson process

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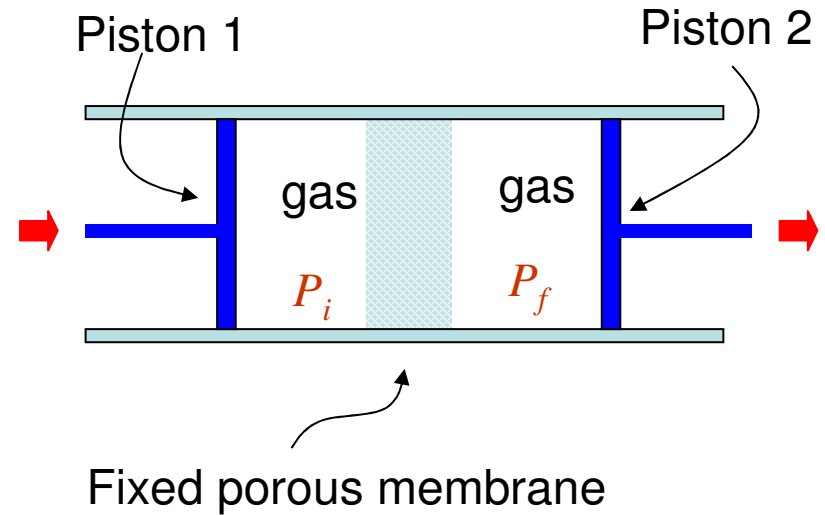
The pistons move to maintain constant pressures  $P_1$  and  $P_2$  in the two regions while the gas is passing through a porous membrane from one region to the other.

The temperature of the gas can be changed by this process as the gas passes from one region to the other.

## The Joule-Thomson process

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Let us consider a situation when one mole of gas was initially in the left region and in the final state was all transferred to the right region.



$v_i$  – initial molar volume

$v_f$  – initial molar volume

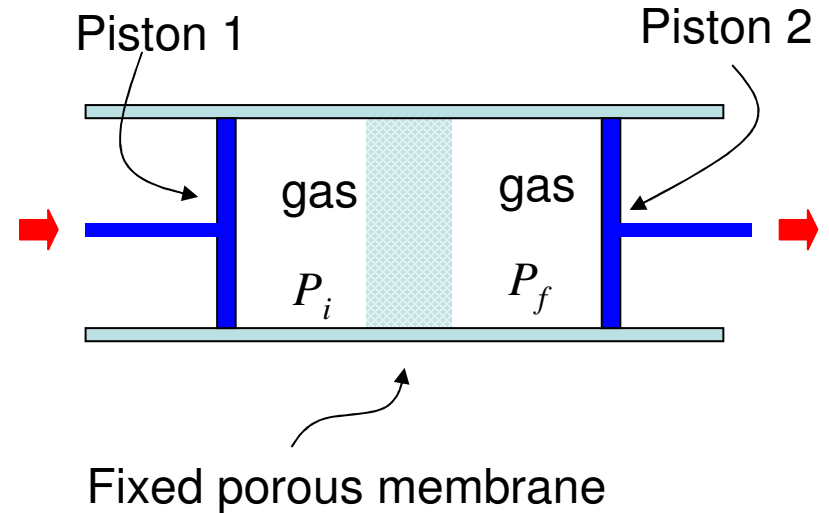
This process is often used for refrigeration.

Note that this is not an equilibrium process!



## The Joule-Thomson process

Since the process is at a constant pressure, work done on the gas by the left piston is  $P_i v_i$ . Work done by the gas on the right piston is  $P_f v_f$ . Since no heat is transferred to the gas from the environment, the internal energy of the gas changes by  $P_i v_i - P_f v_f$ :



$$u_f = u_i + P_i v_i - P_f v_f \quad \Rightarrow \quad u_f + P_f v_f = u_i + P_i v_i \quad \Rightarrow \quad h_f = h_i$$

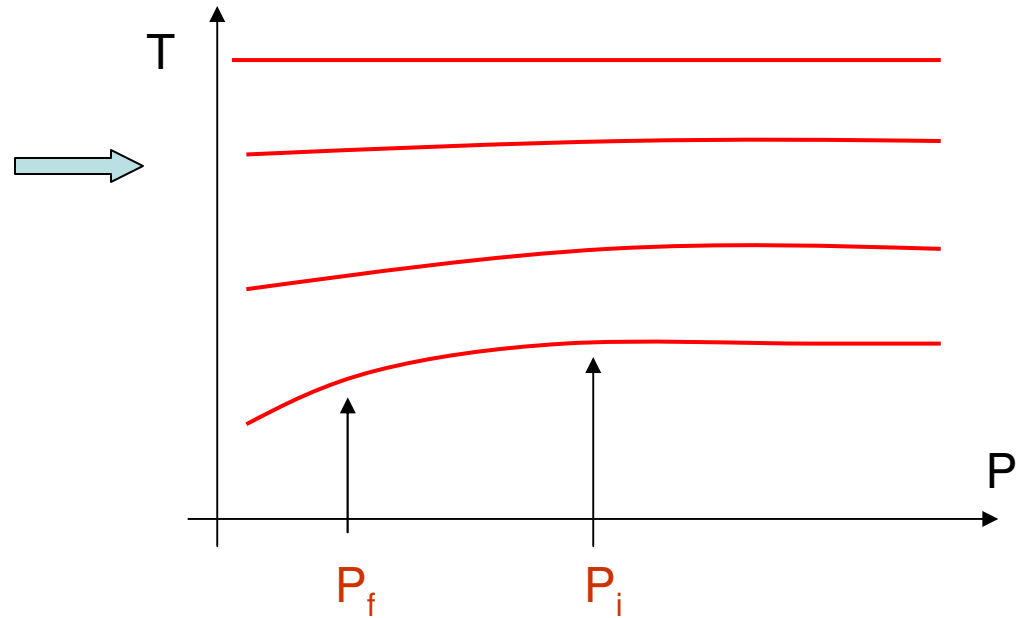
Enthalpy of the initial and final states is the same in the Joule-Thomson process.

## The Joule-Thomson process

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For real gases, curves of constant enthalpy on the  $T$ - $P$  diagram look like this.

Therefore, if we go from the high initial pressure to the low final pressure, the temperature of gas will decrease.



Note that since the process is not equilibrium, the system does not go along the curve of constant enthalpy in the Joule-Thomson process. All the intermediate states of the system are non-equilibrium, only the initial and final states are equilibrium.

## The Gibbs free energy

---

The Gibbs potential  $G(T,P,N,\dots)$  is convenient to use for analysis of processes at constant pressure  $P$  and constant temperature  $T$ .

Most chemical reactions are carried out at ambient pressure and temperature, so  $G$  is the potential of choice for the description of chemical reactions.

$$G = U - TS + PV$$

Substituting the Euler equation in to the expression for  $G$ :

$$U = TS - PV + \mu_1 N_1 + \mu_2 N_2 + \dots \quad \Rightarrow \quad G = \mu_1 N_1 + \mu_2 N_2 + \dots$$

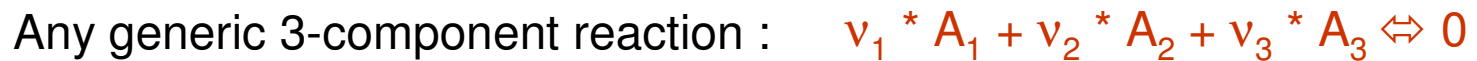
# The Gibbs free energy

---

$$G = \mu_1 N_1 + \mu_2 N_2 + \dots$$

For a single-component system:  $G = \mu N \quad \Rightarrow \quad \mu = \frac{G}{N} = g$

Molar Gibbs free energy for a single-component system = the chemical potential



Here  $v_j$  are stoichiometric coefficients.

## *The Gibbs free energy: chemical reactions*

---

Differential form of the Gibbs free energy:

$$dG = -SdT + VdP + \sum_j \mu_j dN_j$$

Conservation of the total number of each atomic species in chemical reactions demands:

$$dN_j = v_j dN$$

where  $dN$  is the same for all chemical components of the reaction.

## The Gibbs free energy: chemical reactions

---

Therefore:  $dG = -SdT + VdP + dN \sum_j \nu_j \mu_j$

At constant pressure and temperature:  $dG = dN \sum_j \nu_j \mu_j$

In equilibrium,  $dG$  is at minimum at constant pressure and temperature:

$$dG = dN \sum_j \nu_j \mu_j = 0$$

Since  $dN$  is arbitrary:

$$\sum_j \nu_j \mu_j (T, P, N_1, N_2, \dots) = 0 \quad \text{-chemical equilibrium condition}$$

## *The Gibbs free energy: chemical reactions*

---

Let the initial mole numbers of chemicals be:  $N_j^0$

Integrating  $dN_j = \nu_j dN$  we obtain the final mole numbers:

$$N_j^f = N_j^0 + \int dN_j = N_j^0 + \int \nu_j dN = N_j^0 + \nu_j \Delta N$$

Where  $\Delta N$  is simply a numerical factor characterizing the extent of reaction

## The Gibbs free energy: chemical reactions

---

$$N_j^f = N_j^0 + \int dN_j = N_j^0 + \int v_j dN = N_j^0 + v_j \Delta N$$

Where  $\Delta N$  is simply a numerical factor characterizing the extent of reaction

$$\sum_j v_j \mu_j(T, P, N_1, N_2, \dots) = 0 \quad \Rightarrow \quad \sum_j v_j \mu_j(T, P, v_1 \Delta N, v_2 \Delta N, \dots) = 0$$

Since  $T$ ,  $P$  and  $v_j$  are all fixed and known, the chemical equilibrium condition becomes a function of a single parameter characterizing the extent of reaction,  $\Delta N$ . Solving this equation for  $\Delta N$ , we obtain the final mole numbers for the reaction.



## Example: Chemical Reactions in Ideal Gas

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In lecture 5, we considered a model of reaction in an ideal gas

$$S = N \ln(U/U_0) + \sum N_j \ln(N_j/N) \quad \mu_j = -RT \left( \ln(RT / u_0) + \ln(N_j / N) \right)$$

$$\mu_j = -RT \left( \ln(RT / u_0) + \ln(x_j) \right)$$

Then we neglected a term in entropy depending on volume of the gas. If we keep this term and write chemical potential in the Gibbs energy representation:

$$\mu_j = -RT \left( \ln(RT / u_0) + \ln(P) + \ln(x_j) \right)$$

## Example: Chemical Reactions in Ideal Gas

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In a case of generalized ideal gas (not monoatomic), the chemical potential of the  $j^{\text{th}}$  component of a mixture of ideal gases can be written as

$$\mu_j = -RT(\phi_j(T) + \ln(P) + \ln(x_j))$$

where  $\phi_j(T)$  depends on the particular gas and  $x_j$  is molar fraction of the gas

The condition of chemical equilibrium becomes:

$$\sum_j \nu_j \mu_j(T, P, N_1, N_2, \dots) = 0$$
$$\sum_j \nu_j \ln(x_j) = -\sum_j \nu_j \ln(P) - \sum_j \nu_j \phi_j(T)$$

## Example: Chemical Reactions in Ideal Gas

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$$\sum_j \nu_j \ln(x_j) = -\sum_j \nu_j \ln(P) - \sum_j \nu_j \phi_j(T)$$

It is customary to define the equilibrium constant of a reaction  $K(T)$

$$\ln(K(T)) = -\sum_j \nu_j \phi_j(T)$$

With this definition, the equilibrium condition can be written in the form of the **mass action law**:

$$\prod_j x_j^{\nu_j} = P^{-\sum_j \nu_j} K(T)$$

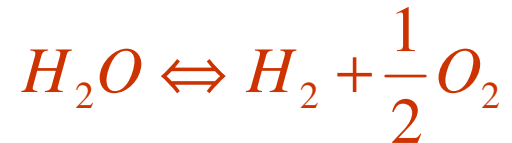
## Example: Chemical Reactions in Ideal Gas

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The mass action law in combination with the conservation of atomic species gives the equilibrium mole fractions for the reacting mixture of gases

**Example:** Consider a reaction of oxygen and hydrogen to form water:

Two moles of water are heated to  $T = 2000 \text{ K}$  at  $P = 1 \text{ MPa}$ . What is the equilibrium composition of the gases in the following reaction?



The equilibrium constant for this reaction is  $K(2000) = 0.0877 \text{ [Pa}^{1/2}\text{]}$

## Example: Thermal Decomposition of Water

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The law of mass action:

$$\prod_j x_j^{v_j} = P^{-\sum_j v_j} K(T)$$

$$\frac{x_{H_2} x_{O_2}^{1/2}}{x_{H_2O}} = P^{-1/2} K(T)$$

Conservation of atomic species gives:

$$N_{H_2O} = 2 - \Delta N$$

$$N_{H_2} = \Delta N$$

$$N_{O_2} = \frac{1}{2} \Delta N$$

## Example: Thermal Decomposition of Water

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The total mole numbers in the reaction:  $N_{H_2O} + N_{H_2} + N_{O_2} = 2 + \frac{\Delta N}{2}$

$$x_{H_2O} = \frac{2 - \Delta N}{2 + \frac{\Delta N}{2}} \quad x_{H_2} = \frac{\Delta N}{2 + \frac{\Delta N}{2}} \quad x_{O_2} = \frac{\frac{1}{2} \Delta N}{2 + \frac{\Delta N}{2}}$$

---

$$\frac{x_{H_2} x_{O_2}^{1/2}}{x_{H_2O}} = P^{-1/2} K(T) \quad \Rightarrow \quad \frac{1}{\sqrt{2}} \frac{\Delta N^{3/2}}{(2 - \Delta N)(2 + \frac{1}{2} \Delta N)^{1/2}} = P^{-1/2} K(T)$$

## Example: Thermal Decomposition of Water

---

$$\frac{1}{2} \frac{\Delta N^3}{(2 - \Delta N)^2 (2 + \frac{1}{2} \Delta N)} = \frac{K^2(T)}{P}$$

This is a cubic equation for  $\Delta N$ . It can either be solved numerically or analytically. The result is  $\Delta N = 0.005$ .

$$x_{H_2O} = 0.9963$$

$$x_{H_2} = 0.0025$$

$$x_{O_2} = 0.0012$$

A simplified solution is obtained if we calculate  $K^2(T)/P$  first.  $K^2(T)/P = (0.0877)^2 10^{-6}$ . From this it is clear that  $\Delta N$  is small and we can write:

$$\Delta N = 2 \left( \frac{2K^2(T)}{P} \right)^{1/3} = 0.005$$