

## The Euler Equation

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Using the additive property of the internal energy  $U$ , we can derive a useful thermodynamic relation – the **Euler equation**.

$$U(\lambda \cdot S, \lambda \cdot V, \lambda \cdot N_1, \dots, \lambda \cdot N_m) = \lambda \cdot U(S, V, N_1, \dots, N_m)$$

Let us differentiate this “extensivity condition” with respect to  $\lambda$ :

$$\begin{aligned} & \frac{\partial U(\lambda \cdot S, \dots)}{\partial(\lambda \cdot S)} \cdot \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U(\lambda \cdot S, \dots)}{\partial(\lambda \cdot V)} \cdot \frac{\partial(\lambda V)}{\partial \lambda} + \frac{\partial U(\lambda \cdot N_1, \dots)}{\partial(\lambda \cdot N_1)} \cdot \frac{\partial(\lambda N_1)}{\partial \lambda} + \dots + \frac{\partial U(\lambda \cdot N_m, \dots)}{\partial(\lambda \cdot N_m)} \cdot \frac{\partial(\lambda N_m)}{\partial \lambda} \\ & = U(S, V, N_1, \dots, N_m) \end{aligned}$$

## The Euler Equation

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$$\frac{\partial U(\lambda \cdot S, \dots)}{\partial(\lambda \cdot S)} \cdot S + \frac{\partial U(\lambda \cdot S, \dots)}{\partial(\lambda \cdot V)} \cdot V + \frac{\partial U(\lambda \cdot N_1, \dots)}{\partial(\lambda \cdot N_1)} \cdot N_1 + \dots + \frac{\partial U(\lambda \cdot N_m, \dots)}{\partial(\lambda \cdot N_m)} \cdot N_m = U(S, V, N_1, \dots, N_m)$$

Setting  $\lambda=1$  in the above equation, we obtain:

$$\frac{\partial U}{\partial S} \cdot S + \frac{\partial U}{\partial V} \cdot V + \frac{\partial U}{\partial N_1} \cdot N_1 + \dots + \frac{\partial U}{\partial N_m} \cdot N_m = U$$

Using the definition of the intensive parameters, we arrive at the **Euler equation**:

$$U = TS - PV + \mu_1 N_1 + \dots + \mu_m N_m$$

## The Gibbs-Duhem Relation

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Extensive thermodynamic coordinates ( $U, S, V, N \dots$ ) are related to each other by the fundamental relation:

Euler equation form of the fundamental relation

$$U = U(S, V, N_1, \dots, N_m) \quad \Rightarrow \quad U = TS - PV + \mu_1 N_1 + \dots + \mu_m N_m$$

It turns out that intensive coordinates (whose number is one less than the number of extensive coordinates counting  $U$ ) are also not all independent from each other. The first differential of the Euler equation (according to the rules of calculus):

we obtain:  $dU = TdS + SdT - PdV - VdP + \mu_1 dN_1 + N_1 d\mu_1 + \dots$

## The Gibbs-Duhem Relation

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$$dU = TdS + SdT - PdV - VdP + \mu_1 dN_1 + N_1 d\mu_1 + \dots$$

Now, if we subtract the most general form of the first differential of the fundamental relation  $U(S, V, \dots)$  from the expression above:

$$dU = \left( \frac{\partial U}{\partial S} \right)_{V, N_1, \dots} dS + \left( \frac{\partial U}{\partial V} \right)_{S, N_1, \dots} dV + \left( \frac{\partial U}{\partial N_1} \right)_{S, V, N_1, \dots} dN_1 + \dots$$

$$dU = TdS - PdV + \mu_1 dN_1 + \dots$$

we derive the **Gibbs-Duhem relation**:

$$SdT - VdP + N_1 d\mu_1 + \dots = 0$$

## Thermodynamic degrees of freedom

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Independent **intensive** thermodynamic coordinates are called thermodynamic degrees of freedom.

The Gibbs-Duhem relation reduced the number of thermodynamic degrees of freedom by one (from the total number of intensive coordinates).

For example, for a single-component gas with **three** intensive coordinates  $T$ ,  $P$  and  $\mu$ , *the number of thermodynamic degrees of freedom is two due to the Gibbs-Duhem relation:*

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP$$

## Thermodynamic degrees of freedom

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$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP$$

If  $S$ ,  $V$  and  $N$  are known as functions of  $T$  and  $P$ , integration of the **Gibbs-Duhem relation** will give  $\mu(T,P)$  as a function of  $T$  and  $P$ .

$$s = \frac{S}{N} \quad v = \frac{V}{N} \quad - \text{molar quantities, independent on } N$$

The idea is that in intensive coordinates, the size of the system is not important (if you know thermodynamic properties of one mole of gas, you know properties of this gas). Excluding the size of the system from consideration reduces the number of degrees of freedom by one.

## Motivation for Gibbs-Duhem Relation in the Entropy Representation

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$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP$$

$$d[T(S, V, N)] \cdot S - d[P(S, V, N)] \cdot V + d[\mu(S, V, N)] \cdot N = 0$$

- Both the Euler equation and the Gibbs-Duhem relation in the energy representation employ **S**, **V** and **N** as thermodynamic coordinates.
- But **S** is not directly measurable in experiment.
- This is why it is useful to write the **Euler equation** and the **Gibbs-Duhem relation** in the **entropy representation** (where the coordinates are **U**, **V** and **N** are measurable).

## Gibbs-Duhem Relation in the Entropy Representation

Now, differentiating the Euler equation in the entropy representation:

$$S = \frac{1}{T}U + \frac{P}{T}V - \frac{\mu}{T}N$$

and subtracting the differential  $dS$ :

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

we obtain the Gibbs-Duhem relation in the entropy representation:

$$U \cdot d\left(\frac{1}{T}\right) + V \cdot d\left(\frac{P}{T}\right) - N \cdot d\left(\frac{\mu}{T}\right) = 0$$

The independent variables in the above expression are **U**, **V** and **N**.  
**U** is easier to measure than **S**.



## Molar parameters

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Sometimes it is convenient to work with molar parameters:

$$s = \frac{S}{N} \text{ - molar entropy} \quad u = \frac{U}{N} \text{ - molar energy} \quad v = \frac{V}{N} \text{ - molar volume}$$

Molar Euler equation

$$S = \frac{1}{T}U + \frac{P}{T}V - \frac{\mu}{T}N \quad \longrightarrow \quad s = \frac{1}{T}u + \frac{P}{T}v - \frac{\mu}{T}$$

Molar Gibbs-Duhem relation

$$U \cdot d\left(\frac{1}{T}\right) + V \cdot d\left(\frac{P}{T}\right) - N \cdot d\left(\frac{\mu}{T}\right) = 0 \quad \longrightarrow \quad u \cdot d\left(\frac{1}{T}\right) + v \cdot d\left(\frac{P}{T}\right) - d\left(\frac{\mu}{T}\right) = 0$$

## *Advantages of using the molar parameters*

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Molar parameter allow us to reduce the number of independent variables in the fundamental relation by one due to the fact that entropy and energy are extensive parameters

$$S(U, V, N) = N \cdot s(U / N, V / N, N / N) = N \cdot s(u, v, 1) \equiv N \cdot s(u, v)$$

We can now write molar entropy as:

$$s = S(U, V, N) / N = s(u, v)$$

We see that molar entropy is only a function of two variables – molar energy and molar volume

## Ideal Gas

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An idealized model of non-interacting gas is called an “ideal gas” if it satisfies the following two equations:

$$PV = NRT \qquad U = cNRT$$

Here  $R$  is the universal gas constant,  $R = N_A k_B$  and  $c$  is a constant.  
 $c = (\text{number of degrees of freedom})/2$

We can rewrite these equations as true equations of state in the entropy representation:

$$\frac{P}{T} = R \frac{N}{V} = \frac{R}{v} \qquad \frac{1}{T} = cR \frac{N}{U} = \frac{cR}{u}$$

## Ideal Gas

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$$\frac{P}{T} = R \frac{N}{V} = \frac{R}{v} \qquad \frac{1}{T} = cR \frac{N}{U} = \frac{cR}{u}$$

We substitute these equations into the **Gibbs-Duhem relation** in the entropy representation:

$$U \cdot d\left(\frac{1}{T}\right) + V \cdot d\left(\frac{P}{T}\right) - N \cdot d\left(\frac{\mu}{T}\right) = 0$$

## Ideal Gas

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Dividing the Gibbs-Duhem relation by  $N$ , we obtain:

$$u \cdot d\left(\frac{1}{T}\right) + v \cdot d\left(\frac{P}{T}\right) = d\left(\frac{\mu}{T}\right)$$

Substituting the equations of state:  $\frac{1}{T} = cR \frac{N}{U} = \frac{cR}{u}$        $\frac{P}{T} = R \frac{N}{V} = \frac{R}{v}$

$$u \cdot d\left(\frac{cR}{u}\right) + v \cdot d\left(\frac{R}{v}\right) = d\left(\frac{\mu}{T}\right) \quad \longrightarrow \quad -u \cdot \frac{cR}{u^2} du - v \cdot \frac{R}{v^2} dv = d\left(\frac{\mu}{T}\right)$$

## Ideal Gas

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$$-u \cdot \frac{cR}{u^2} du - v \cdot \frac{R}{v^2} dv = d\left(\frac{\mu}{T}\right) \quad \Rightarrow \quad -cR \cdot d \ln(u) - R \cdot d \ln(v) = d\left(\frac{\mu}{T}\right)$$

Integrating:

$$-cR \ln(u) - R \ln(v) = \frac{\mu}{T} + \text{const}$$

This is third equation of state.



## Ideal Gas

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Now we can substitute all three equations of state into the molar form of the Euler equation in the entropy representation :

$$s = \left(\frac{1}{T}\right)u + \left(\frac{P}{T}\right)v - \left(\frac{\mu}{T}\right)$$

to obtain the fundamental relation

$$s = cR + R + cR \ln(u) + R \ln(v) + const$$

Note that this equation does not work at small  $u$  and  $v$  since  $s$  becomes negative

## Ideal Gas: Alternative Method

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We can use the fact that entropy is an *extensive* coordinate:

$$S = S(U, V, N) = N \cdot S(U/N, V/N, 1) = N \cdot s(u, v) \quad \longrightarrow \quad s = S/N = s(u, v)$$

Therefore:  $ds = \frac{1}{T} du + \frac{P}{T} dv$       or       $ds = \frac{cR}{u} du + \frac{R}{v} dv$

This expression can be directly integrated to give:

$$s = cR \ln(u) + R \ln(v) + \text{const}$$