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Minimum requirements for **underneath of your pillow**. However, **write your own summary!** You need to know the story behind the equations...

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T: Pressure

V: Volume

n: particle number

 $T_{\text{trip}}$ : temperature of triple point of water

R: Gas constant

 $\alpha$ : phase of a system $\gamma^0$ : standard value of a therm. function (1 bar, and typically at room temperature)

X: mole fraction

 $P_c$ : pressure at critical point**Be aware of typos.****IDEAL GAS** (no interactions no volume of the species)

(More realistic equations such as the van der Waals equation include the interaction of the particles and there volume.)

Boyl's law

$$V \propto 1/p \text{ for } n \ \& \ T = \text{constant}$$

Gay-Lussac &amp; Charles laws

$$\begin{cases} V \propto T \text{ for } n \ \& \ P = \text{constant} \\ p \propto T \text{ for } n \ \& \ V = \text{constant} \end{cases}$$

Avogadro's law

$$V \propto n \text{ for } P \ \& \ T = \text{constant}$$

Equal volumes of different gases have equal numbers of particles if T and p are constant. Or, p, V, T = const (i.e. are the same for two different gases) then the number of particles n is the same.

General ideal gas equation

$$PV = nRT$$

Dalton's law

$$P_{\text{tot}} = P_1 + P_2 + P_3 + \dots$$

A reversible process is

- one where a system is always infinitesimally close to equilibrium,
- and an infinitesimal change in conditions can reverse the process to restore both system and surroundings to their initial states.

Extensive properties are equal to the sum of their values (e.g. volume, mass, heat,  $c_p$ ). Intensive properties do not depend on the amount of matter (e.g. temperature, density).

## THERMODYNAMIC FUNCTIONS

mechanical work

$$w = \int_{\vec{r}_1}^{\vec{r}_2} \vec{F}(\vec{r}) d\vec{r}$$

pressure work

$$w_{tot} = \int_1^2 dw = - \int_1^2 P dV$$

heat capacities

$$c_P = \left( \frac{dq}{dT} \right)_{P=const}; c_V = \left( \frac{dq}{dT} \right)_{V=const}$$

$$c_P = \left( \frac{\partial H}{\partial T} \right)_{P=const}; c_V = \left( \frac{\partial U}{\partial T} \right)_{V=const}$$

$$c_V - c_P = nR \text{ (ideal gas)}$$

Enthalpy

$$\begin{cases} H := U + PV \\ \Delta H = q \text{ for } P = \text{constant} \\ \Delta U = q \text{ for } V = \text{constant} \end{cases}$$

adiabatic expansion

(Joule-Thomson, Linde apparatus for liquefying air, fast expansion of a gas, open suddenly a gas cylinder without a regulator – don't do that at home)

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{R/c_V}; P_1 V_1^\gamma = P_2 V_2^\gamma; \gamma = c_P/c_V$$

compare  $pV \propto \text{const}$  (Boyle's law) with  $pV^\gamma \propto \text{const}$  (Poisson eq)

state functions

(e.g. U, Cp, Cv)

$$\int_1^2 db = \Delta b = b_2 - b_1; \oint db = 0$$

$\Delta b$  is independent of the way from initial (1) to final (2) state

non state functions

$$\int_1^2 dq = q \quad (\text{e.g. } q, w)$$

Entropy

$$dS = \frac{dq}{T}; dS = \left(\frac{\Delta H}{T}\right)_{T \& P = \text{const}}$$

(What is difference between dS and C<sub>p</sub>?)

Gibbs equation

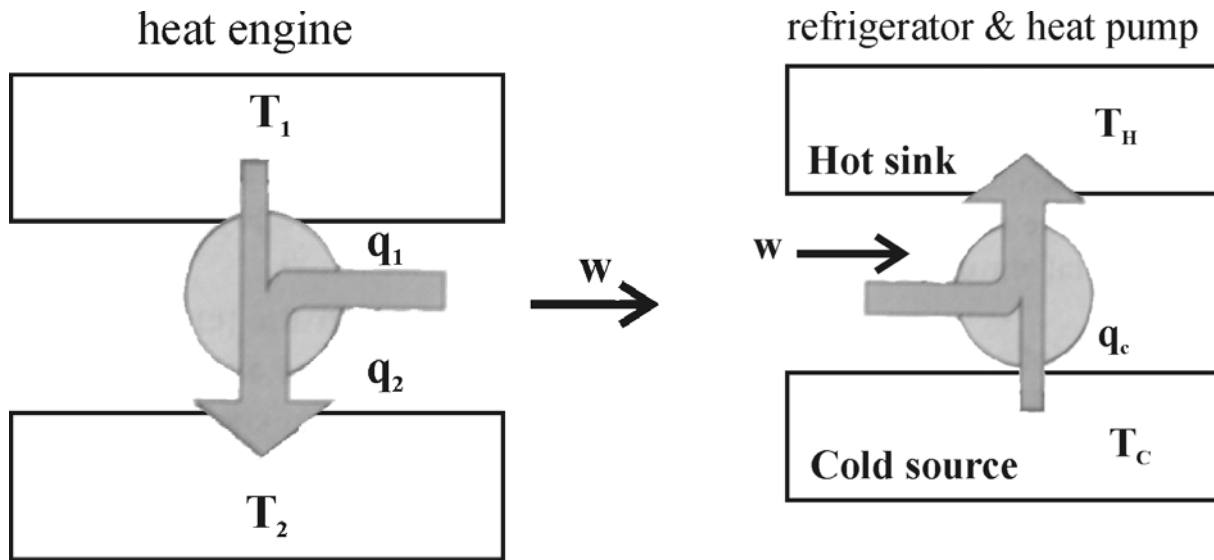
$$dG = VdP - SdT + \sum_{\alpha} \sum_{i=1}^k \mu_i^{\alpha} dn_i^{\alpha}$$

Important definitions:

Enthalpy  $H = U + PV$

Helmholz free energy  $A = U - TS$

Gibbs energy  $G = H - TS$



$$\eta = 1 + \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

Coefficient of performance

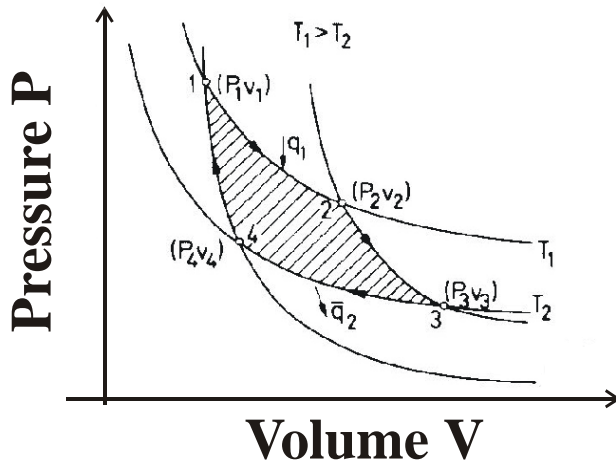
refrigerator  $K = q_c/w$

heat pump  $e = -q_h/w$

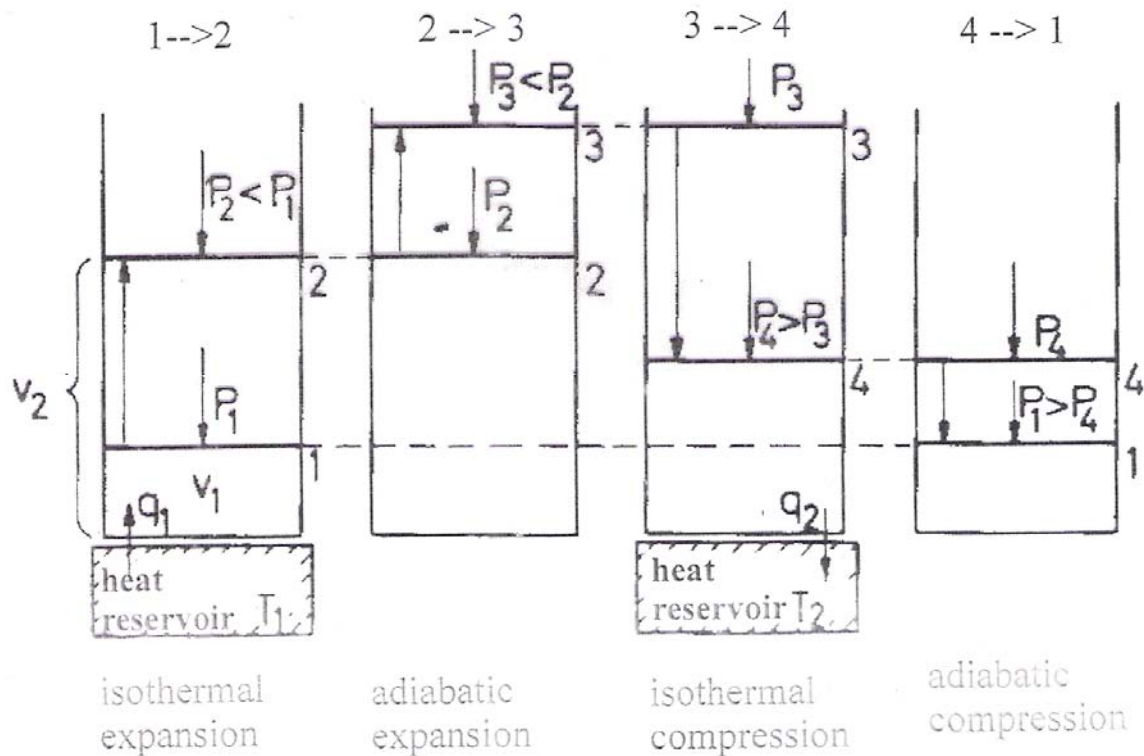
# Carnot cycle

Cycles: 2x isothermal and 2x adiabatic

$$\eta = \frac{\text{work output}}{\text{heat input}} = 1 + \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$



	heat	work
1 --> 2	$q_1 = q_{12} = -RT_1 \ln(V_2/V_1)$	$w_{12} = -q_1$
isothermal		
2 --> 3	$q_{23} = 0$	$w_{23} = -c_V(T_2 - T_1)$
adiabatic		
3 --> 4	$q_2 = q_{34} = -RT_2 \ln(V_4/V_3)$	$w_{34} = -q_2$
isothermal		
4 --> 1	$q_{41} = 0$	$w_{41} = -c_V(T_1 - T_2)$
adiabatic		



Note that the equation  $w_{23} = -c_V \Delta T$  for an adiabatic step is very useful for analyzing these cycles (see above and try to remember that). (Why?:  $\Delta U = c_V \Delta T$  for an ideal gas – that is basically the definition of an ideal gas-, 1<sup>st</sup> law  $\Delta U = w + q$ , adiabatic step  $q = 0$ ).

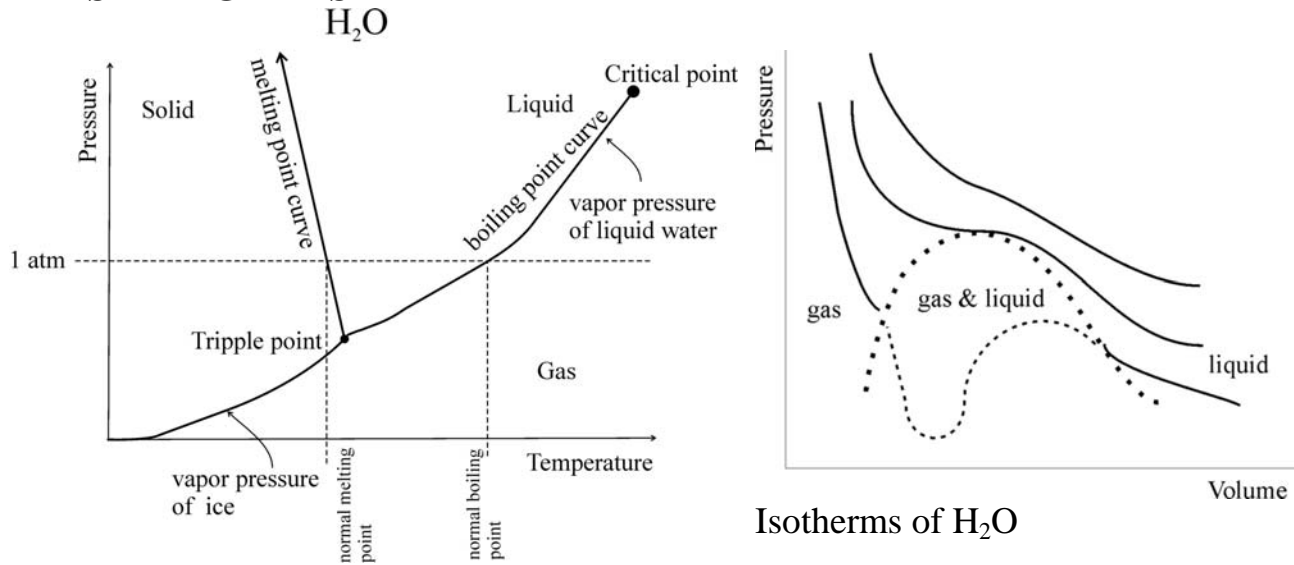
# MATERIAL EQUILIBRIUM

$$dS_{\Sigma} = dS_{system} + dS_{surrounding} = \begin{cases} = 0 & \text{reversible} \\ > 0 & \text{irreversible} \end{cases} \bigg\} process$$

A:=U-TS (Helmholts free energy)	G:=H-TS (Gibbs free energy)
cf., maximum work for V = const process (Arbeitsfunktion = thermodynamic work function)	cf., maximum work for P = const process
dA = 0 at equilibrium for T&V = constant	dG = 0 at equilibrium for T&P = constant
chemical potential	$\mu_i^{\alpha} = \left( \frac{\partial G^{\alpha}}{\partial n_i^{\alpha}} \right)_{T=const, P=const}$ <p>all mole numbers except <math>n_{i \neq j}^{\alpha} = \text{const}</math></p>
$\sum_{\alpha} \sum_{i=1}^k \mu_i^{\alpha} dn_i^{\alpha} = 0 \quad T \& P = \text{const or } @ T \& V = \text{const}$	
<p>phase equilibrium</p> $\mu_i^{\alpha} = \mu_i^{\beta}$ <p><math>\mu</math> of species i is the same in every phase that contains i In approaching the equilibrium: i flows from phase with larger <math>\mu</math> to phase with lower <math>\mu</math>.</p>	<p>reaction equilibrium</p> $\nu_1 A_1 + \nu_2 A_2 + \dots \rightarrow \nu_m A_m + \nu_{m+1} A_{m+1} + \dots$ $\sum_i \nu_i \mu_i = 0$

$$\mu_i = \mu_i^0 + RT \ln(P_i/P^0) \text{ (ideal gas)}$$

## PHASE DIAGRAMS



**Phase rule:**  $f = pc + 2 - p - c(p - 1) - r - a$

f: degree of freedom; constraints: number of p: phases; c: species; r: reactions; a: other restrictions such as stoichiometry, conservation of charge

Example: H<sub>2</sub>O solid phase region (f = 2); liquid-gas equilibrium (f = 1).

$T > T_c \rightarrow \text{density (liquid)} = \text{density (gas)}$

$\Delta H_m^{\text{vap}} \rightarrow 0 \text{ for } T \rightarrow T_c$

**Clausius-Clapeyron**  $\frac{d \ln P}{dT} \approx \frac{\Delta H}{RT^2} ; \ln\left(\frac{P_2}{P_1}\right) \approx -\frac{\Delta H_m}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

**Metastable phase**  $G_\alpha > G_\beta$  leads to a slow phase change  $\alpha \rightarrow \beta$

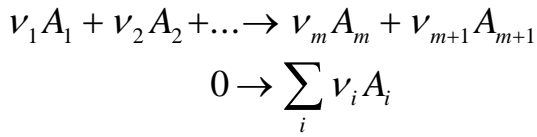
example: diamond  $\rightarrow$  graphite

**Phase transitions** (Ehrenfest classification)

1<sup>st</sup> order:  $\frac{\partial \mu}{\partial T}$  is discontinuous

2<sup>nd</sup> order:  $\frac{\partial \mu}{\partial T}$  is discontinuous and  $\frac{\partial^2 \mu}{\partial^2 T}$  is discontinuous

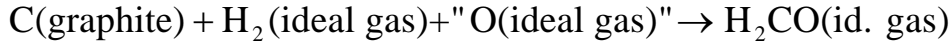
## STANDARD THERMODYNAMIC FUNCTIONS



Standard enthalpy of formation

$$\Delta H^0 = \sum_i \nu_i \Delta H_f^0$$

Def.:  $\Delta H_f^0$  is the enthalpy change for isothermally ( $T = \text{const}$ ) conversion of pure elements in their reference forms (typically their most stable forms) to a standard-state substance. Standard state is typically 1 atm & 25C.



e.g.  $\Delta H^0 = \Delta H_f^0(\text{H}_2\text{CO}) = \Delta H_f^0(\text{graphite}) + \Delta H_f^0(\text{H}_2 \text{ ideal gas}) + \Delta H_f^0(\text{oxygen id. gas})$

**Hess's law:** elements +  $\text{O}_2 \rightarrow$  combustion product  $\rightarrow$  desired molecule +  $\text{O}_2$

We need  $\Delta_f H^0$  for a product that cannot be synthesized from its elements.  $H$  is a state function, i.e., we can add chemical equations and the corresponding  $\Delta_f H^0$  together.

### Kirchhoff's law

(problem we know  $\Delta H_0(T_1)$   
we need  $\Delta H_0(T_2)$ )

$$\Delta H_{T_2}^0 - \Delta H_{T_1}^0 = \int_{T_1}^{T_2} \Delta C_p^0 dT$$

Entropy

$$\Delta S_T^0 = \sum_i \nu_i S_{m,T,i}^0$$

Gibbs energy

$$\Delta G_T^0 = \sum_i \nu_i G_{m,T,i}^0$$

## LAWS OF THERMODYNAMICS

### 0<sup>th</sup> law

Definition of the temperature.

$$T = \lim_{P \rightarrow 0} T(P); T(P) = \frac{P}{P_{trip}} T_{trip} \text{ (Gas thermometer)}$$

### 1<sup>st</sup> law

$$\Delta E = q + w; \text{ system at rest: } \Delta U = q + w$$

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

A 2<sup>nd</sup> order “perpetuum mobile” does not exist. It is impossible to build a cyclic machine which converts heat into work with an efficiency of 100 %. The total entropy is increasing in any irreversible process  $\Delta S \geq 0$ .

### 3<sup>rd</sup> law

$$\text{Part A: } \lim_{T \rightarrow 0K} \left( \frac{\partial \Delta G}{\partial T} \right)_P = 0; \quad \lim_{T \rightarrow 0K} \Delta S = 0$$

(Leads to the definition of a standard entropy.)

Part B: Unattainability principle: The absolute zero temperature 0 Kelvin cannot be reached.

## GAS MIXTURES.

Chemical potential

$$\mu_1 = \mu_i^0 + RT \ln(P_i / P^0)$$

Equilibrium constant

$$\Delta G^0 = -RT \ln(K_p^0) \text{ with } K_p^0 := \frac{\prod_{products} (P_i / P^0)^\nu}{\prod_{reactants} (P_j / P^0)^\nu}; K_p^0 = e^{-\Delta G^0 / RT}$$

van't Hoff equation

$$\frac{d \ln(K_p^0)}{dT} = \frac{\Delta H^0}{RT^2}$$

$$\ln\left(\frac{K_p^0(T_2)}{K_p^0(T_1)}\right) \approx \frac{\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$



## SOLUTIONS

Partial molar volume

$$\bar{V}_j = \left( \frac{\partial V}{\partial n_j} \right)_{T, P, n(i \neq j) = \text{const}}$$

Total volume

$$V = \sum_j n_j \bar{V}_j \quad (\text{obeyed or all extensive properties of a solution})$$

Important equations

$$\frac{\partial \Delta_{\text{mix}} G}{\partial P} = \Delta_{\text{mix}} V; \quad \frac{\partial \Delta_{\text{mix}} G}{\partial T} = -\Delta_{\text{mix}} S$$

Ideal solution

$$\text{def. } \mu_i = \mu_i^{\text{pure}}(T, P) + RT \ln(x_i)$$

$$\Delta_{\text{mix}} S = -R \sum_i n_i \ln(x_i); \quad \Delta_{\text{mix}} G = RT \sum_i n_i \ln(x_i);$$

$$\Delta_{\text{mix}} H = 0; \quad \Delta_{\text{mix}} U = 0$$

**Raoult's law** The ratio of the partial vapor pressure of each component of the solution to the corresponding vapor pressure of the pure liquids is equal to the mole fraction of that component in the liquid mixture.

$$\frac{\text{vapor pressure of A in the solution}}{\text{vapor pressure of pure A}} = \text{mole fraction of A}$$

$$P_i = X_i^{\text{liquid}} P_i^{\text{pure}}$$

Ideally dilute solution

$$X_{\text{solvent}} \rightarrow 1$$

$$\mu_{\text{solute}} = \mu_{\text{solute}}^0(T, P) + RT \ln(x_{\text{solute}})$$

$$\mu_{\text{solvent}} = \mu_{\text{solvent}}^0 + RT \ln(x_{\text{solvent}})$$

Henry's law

$$P_{\text{solute}} = \text{Const}_{\text{solute}} X_{\text{solute}}^{\text{liquid}} \quad (\text{Raoult's law is obeyed for the solvent})$$

**useful but not necessarily to memorize:**

Gibbs equations

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

Thermal expansion coefficient

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P \& V = \text{const}} \quad \left( \frac{\partial P}{\partial T} \right)_{V_m} = \frac{\alpha}{\kappa}$$

Isothermal compressibility

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T \& n = \text{const}}$$

(for an ideal gas  $\alpha = \frac{1}{T}$ ;  $\kappa = \frac{1}{P}$ )

Joule Thomson experiment (adiabatic expansion of a gas,  $\Delta H = 0$ )

$$\mu = \left( \frac{\partial T}{\partial p} \right)_H = \frac{T \left( \frac{\partial V}{\partial T} \right)_P - V}{C_p} = \begin{cases} > 0 \text{ for } T < T_i \text{ "cooling"} \\ < 0 \text{ for } T > T_i \text{ "heating"} \end{cases}$$

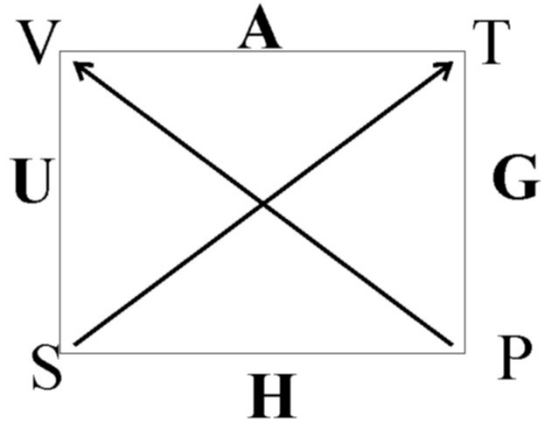
$$T_i = \frac{2a}{Rb} \text{ (inversion temperature), for He well below room temperature}$$

Maxwell Relations

$$\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V \quad \left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P$$

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad \left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P$$

That scheme helps to remember the partial derivatives of the thermodynamic potentials



- 1) Choose one of the potentials (e.g. U),
  - 2) choose the denominator (e.g. S)
  - 3) go to the other side of the square and find the parameter kept constant (e.g. V)
  - 4) go along the arrow starting at the position of the denominator (e.g. S)
  - 5) and you will find the partial derivative  $(\partial U / \partial S)_V = T$
- (Note: going along the arrow +, in the opposite direction -)

V: Volume  
T: Temperature  
P: Pressure  
S: Entropy

A: Helmholtz free energy  
G: Gibbs energy  
H: Enthalpy  
U: internal energy

$$\begin{aligned} \left(\frac{\partial U}{\partial S}\right)_V &= T & \left(\frac{\partial U}{\partial V}\right)_S &= -P \\ \left(\frac{\partial A}{\partial T}\right)_V &= -S & \left(\frac{\partial A}{\partial V}\right)_T &= -P \\ \left(\frac{\partial G}{\partial T}\right)_P &= -S & \left(\frac{\partial G}{\partial P}\right)_T &= V \\ \left(\frac{\partial H}{\partial S}\right)_P &= T & \left(\frac{\partial H}{\partial P}\right)_S &= V \end{aligned}$$

## Mixing entropy

$$\Delta_{mix} S = - \sum_i n_i R \ln(x_i);$$

$n_i$ : mole fraction

The entropy of an ideal gas mixture is equal to the sum of the entropies each pure gas would have if it alone occupied the volume of the mixture (at the temperature of the mixture). Follows basically from Daltons law ( $P_{tot} = P_1 + P_2 + P_3 + \dots$ ).

## REAL GASES

Van der Waals equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Compression factor

$$Z(P, T) = \frac{pV_m}{RT} = \frac{V_m}{V_m^{ideal}}$$

ideal gas  $pV = nRT$

real gas  $pV = ZRT$

$Z(P, T)$ : compression factor

Virial equation

$$PV = RT(1 + B/V + C/V^2 + D/V^3 + \dots)$$

Maxwell construction ...

Law of corresponding states: If we define reduced parameters (e.g.  $P_r = P/P_c$ ) then  $V_r$  equals approximately  $f(P_r, T_r)$  for all gases.