## Lover

0. 
$$A \sim B$$
 og  $B \sim C$  gir  $A \sim C$ 

1. 
$$\Delta E = Q + W$$

2. 
$$\Delta S \ge 0$$
 Isolert system

3. 
$$\lim_{T\to 0} \Rightarrow S = \text{konstant}$$

# Mye brukte formler

$$F = E - TS$$
 Helmholtz  $G = E - TS + PV$  Gibbs

$$F = -kT \ln(Z)$$

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT$$

$$\ln N! \approx N \ln N - N$$

$$S \equiv k \ln \Omega$$

$$\Delta S_{\text{mixing}} = k \ln \binom{N}{N_A}$$

$$W_{AB} = W_B - W_A = \int_{V_A}^{V_B} P(V)DV$$

$$E = -kT^2 \left(\frac{\partial \ln Z}{\partial T}\right)$$

# Ideell gass

$$PV = NkT$$

$$\bar{n}_{BE} = \frac{1}{\exp[(\epsilon - \mu)/kT] - 1}$$

$$\Delta S = \frac{dE}{T} = \frac{Q}{T} = \frac{C_V dT}{T}$$

$$\bar{n}_B = \exp[-(\epsilon - \mu)/kT]$$

$$S = Nk \left[ \ln\left(\frac{V}{N} \left(\frac{4\pi mE}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2} \right]$$

$$E = \int_0^\infty \epsilon \bar{n}(\epsilon, \mu, T) D(\epsilon) d\epsilon$$

$$N = \int_0^\infty \bar{n}(\epsilon, \mu, T) D(\epsilon) d\epsilon$$

## Multiplisitet

$$\Omega(N_{\uparrow}) = \binom{N}{N_{\uparrow}} = \frac{N!}{N_{\uparrow}! N_{\downarrow}}$$
 Paramagnet 
$$\Omega(N, q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!}$$
 Einsteinkrystall

$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{(3N/2-1)!} (\sqrt{2mE})^{3N-1}$$
 Ideell gass

# Varmeutveksling

$$\begin{array}{ll} e & \equiv \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} & \text{Effektivitet varmemaskin} \\ e & \equiv \frac{Q_c}{W} = \frac{1}{Q_h/Q_c - 1} & \text{Effektivitet kjølemaskin} \\ \frac{dP}{dT} & = \frac{S_g - S_l}{V_g - V_l} = \frac{L}{T\Delta V} & \text{Clausius-Clapeyron} \end{array}$$

### Kanonisk

$$P=rac{1}{Z}\exp(-\epsilon_i/kT)$$
 Boltzmannsfordelingen 
$$Z=\sum_i\exp(-\epsilon_i/kT)$$
 Partisjonsfunksjonen 
$$Z_N=rac{Z_1^N}{N!}$$
 Total partisjon

#### Grand-kanonisk

$$\mathcal{Z} = \sum_{i} \exp{-[\epsilon_{i} - N\mu]/kT} \qquad \text{Gibbs sum}$$
 
$$\bar{n}_{FD} = \frac{1}{\exp[(\epsilon - \mu)/kT] + 1} \qquad \text{Fermi-Dirac}$$
 
$$\bar{n}_{BE} = \frac{1}{\exp[(\epsilon - \mu)/kT] - 1} \qquad \text{Bose-Einstein}$$
 
$$\bar{n}_{B} = \exp[-(\epsilon - \mu)/kT] \qquad \text{Boltzmann}$$
 
$$E = \int_{0}^{\infty} \epsilon \bar{n}(\epsilon, \mu, T) D(\epsilon) d\epsilon$$
 
$$N = \int_{0}^{\infty} \bar{n}(\epsilon, \mu, T) D(\epsilon) d\epsilon$$

# Begreper

#### Isokor

Romlige dimensjoner (Volum, areal, lengde) holdes konstant

#### Isoterm

Temperaturen holdes konstant

#### Isobar

Trykket holdes konstant

#### Kvasistatisk

En prosess som skjer så sakte at systemet blir værende i likevekt.

#### Adiabatisk

Ingen endring i varme, i de fleste tilfeller heller ingen endring i entropi.

# Isentropisk

Adiabatisk og kvasistatisk

#### Likevekt

- Mekanisk likevekt dP = 0
- Termisk likevekt dT = 0
- Diffusiv likevekt  $d\mu = 0$
- Kjemisk likevekt dG = 0

# Maxwellrelasjoner

Relasjoner bygget på Schwarz' teorem:

$$\frac{\partial}{\partial x} \left( \frac{\partial f}{\partial y} \right) = \frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right)$$

#### Eksempler:

$$\begin{split} & + \left(\frac{\partial T}{\partial V}\right)_S = & - \left(\frac{\partial P}{\partial S}\right)_V \\ & + \left(\frac{\partial T}{\partial P}\right)_S = & + \left(\frac{\partial V}{\partial S}\right)_P \\ & + \left(\frac{\partial S}{\partial V}\right)_T = & + \left(\frac{\partial P}{\partial T}\right)_V \\ & - \left(\frac{\partial S}{\partial P}\right)_T = & + \left(\frac{\partial V}{\partial T}\right)_P \end{split}$$

## Nyttige sammenhenger:

- Konstant energi og volum  $\Rightarrow \Delta S > 0$
- Konstant temperatur og volum  $\Rightarrow \Delta F < 0$
- Konstant temperatur og trykk  $\Rightarrow \Delta G < 0$

# Differensialer

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial E}\right)_{N,V}$$

$$C_V \equiv \left(\frac{\partial E}{\partial T}\right)_{N,V}$$

$$P = +T\left(\frac{\partial S}{\partial V}\right)_{E,N} = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{E,V} = +\left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

$$S = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$$

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$$

# Identiteter

$$dE = TdS - PdV + \mu dN$$
  

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

$$dG = -SdT + VdP + \mu dN$$

# Utledninger

# Den termodynamiske identitet

- 1. Tar utgangspunkt i dQ = TdS
- 2. T1L: dE = dQ + dW
- 3.  $dW = PdV = \sigma dA = KdX$
- 4. Kan legge til  $\mu dN$

$$\Rightarrow TdS = dE - PdV + \mu dN$$

## Energi rett fra Z

Utgangspunkt:

$$Z(N, V, T) = \sum_{i}^{N} \exp(-\epsilon_i/kT)$$
$$P = (1/Z) \exp(-\epsilon_i/kT)$$

$$E = \sum_{i}^{N} \epsilon_{i} P(\epsilon_{i}) = (1/Z) \sum_{i}^{N} \epsilon_{i} \exp(-\epsilon_{i}\beta)$$
$$= \frac{1}{Z} \sum_{i}^{N} -\frac{\partial}{\partial \beta} \exp(-\epsilon_{i}\beta) = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$
$$= -\frac{d \ln Z}{d\beta} = kT^{2} \left(\frac{\partial \ln Z}{\partial T}\right)$$

### Adiabat for ideell gass

- 1. Ta utgangspunkt i Sackur-Tetrode
- 2. Adiabat  $dS = 0 \Rightarrow S_1 = S_2$
- 3. Bruk ekvipartisjonsprinsippet  $\Rightarrow V_1^{2/3}T_1 = V_2^{2/3}T_2$

## Clausius-Clapeyron

- 1.  $G_l = G_q$
- 2.  $G_l(P_0 + dP, T_0 + dT) = G_g(P_0 + dP, T_0 + dT)$
- 3. Taylor:

$$G_l(P_0+dP,T_0+dT) \approx G_l(P_0,T_0)$$

$$+ \left(\frac{\partial G_l}{\partial P}\right) dP + \left(\frac{\partial G_l}{\partial T}\right) dT$$

4. Bruker differensialene

$$\left(\frac{\partial G_l}{\partial P}\right)_T = V_l, \quad \left(\frac{\partial G_l}{\partial T}\right)_P = -S_l$$

$$\Rightarrow V_l dP - S_l dT = V_q dP - S_q dT$$

$$\Rightarrow \frac{dP}{dT} = \frac{S_l - S_g}{V_l - V_g} = \frac{L(T)}{T\Delta V}$$

# Bose-Einstein-fordelingen

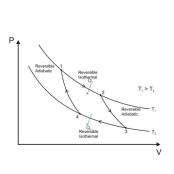
1. Tar utgangspunkt i

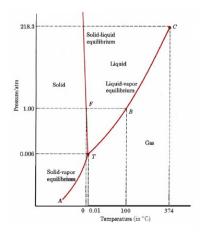
$$\mathcal{Z} = \sum_{i}^{N} \exp[-(n\epsilon - n\mu)/kT]$$

- 2. Bruker at n = 1, 2, 3...
- 3. Bruker  $\sum_{n} q^2 = 1/(1-q), q < 1$
- 4.  $\bar{n} = \sum nP(n)$

$$\Rightarrow \frac{1}{\mathcal{Z}} \sum_{n} n \exp(-nx) = \frac{1}{\mathcal{Z}} \sum_{n} \frac{\partial}{\partial x} \exp(-nx)$$

$$\Rightarrow \frac{1}{Z} \frac{\partial Z}{\partial x} = \frac{1}{\exp[(\epsilon - \mu)/kT] - 1}$$





- (a) Carnotsyklusen
- (b) Faseoverganger for rene substanser

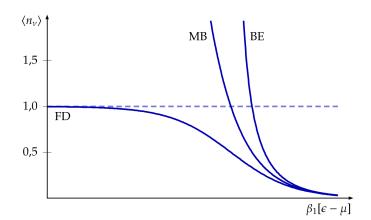


Figure 1: Fordelingsfunksjoner (Fermi-Dirac, Boltzmann, Bose-Einstein)

# Tilstandstettheten og fermienergi 3D:

$$D(n)dn = N_T \cdot A = 2 \cdot (1/8) \cdot 4\pi n^2 dn = \pi n^2 dn \qquad N_T = 2 \text{ for fermioner}$$

$$\Rightarrow D(n)dn = D(\epsilon)d\epsilon \Rightarrow D(\epsilon) = \pi n^2 (1/2an) = \frac{\pi}{2a}n = \frac{\pi}{2a}\sqrt{\frac{\epsilon}{a}}$$

$$N = N_T \cdot V(n_{max}) = 2 \cdot \frac{1}{8} \cdot \frac{4}{3}\pi n_{max}^3 \quad \Rightarrow n_{max}^2 = \left(\frac{3N}{\pi}\right)^{2/3}$$

$$\epsilon_F = \epsilon(n_{max}) = an_{max}^2 = a\left(\frac{3N}{\pi}\right)^{2/3}$$