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# **Thermodynamics and Statistical Mechanics**

**Thermodynamics IV**  
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- **Thermodynamic potentials**
- **Enthalpy**
- **Helmholtz free energy**
- **Gibbs free energy**
- **Chemical potential**
- **Landau free energy**

# THERMODYNAMIC POTENTIALS

Thermodynamic systems may do work on their environments

Under certain constraints  $\Rightarrow$  work done may be bounded from above  
by change in appropriately defined **thermodynamic potential**

Imagine creating

thermodynamic system from scratch in thermally insulated box of volume  $V$

Work to assemble system  $\Rightarrow \mathcal{W} = U$

After bringing together all particles from infinity system has internal energy  $U$

System however  $\Rightarrow$  may not be in thermal equilibrium

Spontaneous processes will then occur so as to maximize system's entropy

but internal energy remains @  $U$

Combining  $\left\{ \begin{array}{l} \text{First Law} \quad dU = \delta Q - \delta W \quad \Rightarrow \quad U(S, V) \\ \text{Main thermodynamics identity} \quad dU = TdS - PdV \end{array} \right.$

it follows that  $T = \left( \frac{\partial U}{\partial S} \right)_V$  and  $-P = \left( \frac{\partial U}{\partial V} \right)_S$

Second Law in form  $\delta Q \leq TdS$  yields  $\Rightarrow dU \leq TdS - PdV$

## FREE WORK

For process @ fixed  $(S, V) \Rightarrow dU \leq 0$

This says spontaneous processes in system with  $dS = dV = 0$   
always lead to reduction of internal energy

In systems @ fixed  $(S, V)$   
spontaneous processes drive internal energy  $U$  to a minimum

Allowing for other work processes  $\Rightarrow \delta W \leq TdS - dU$

Work done by system under thermodynamic conditions of constant entropy  
is bounded above by  $-dU$   
and maximum  $\delta W$  is achieved for reversible processes

It is useful to define  $\Rightarrow \delta W_{\text{free}} = \delta W - PdV$

which is differential work done by system other than required to change  $V$

It follows that  $\Rightarrow \delta W_{\text{free}} \leq TdS - PdV - dU$

CONCLUSION: for systems @ fixed  $(S, V) \Rightarrow \delta W_{\text{free}} \leq -dU$

# THE LEGENDRE TRANSFORMATION

Consider function  $Z = Z(x, y)$  and compute differential

$$dZ(x, y) = Xdx + Ydy \quad (\text{A})$$

$x, X$  and  $y, Y$  are (by definition) canonically conjugate pairs

To replace  $(x, y)$  by  $(X, Y)$  as independent variables

transform  $Z = Z(x, y)$  according to

$$M(X, Y) = Z - xX - yY$$

it follows that  $\Rightarrow dM = dZ - Xdx - Ydy - x dX - y dY \quad (\text{B})$

Substituting (A) into (B)  $\Rightarrow dM = -x dX - y dY \quad (\text{C})$

(A) and (C) give reciprocity relations:

$$\frac{\partial Z}{\partial x} = X, \quad \frac{\partial Z}{\partial y} = Y, \quad \frac{\partial M}{\partial X} = -x, \quad \frac{\partial M}{\partial Y} = -y$$

## THE LEGENDRE TRANSFORMATION II

To replace only one of the variables transform according to

$$N(x, Y) = Z - yY \quad (\text{D})$$

it follows that

$$dN = dZ - Y dy - y dY \quad (\text{E})$$

Substituting (A) into (E)  $\rightarrow$   $dN = X dx - y dY$

with reciprocity relations:

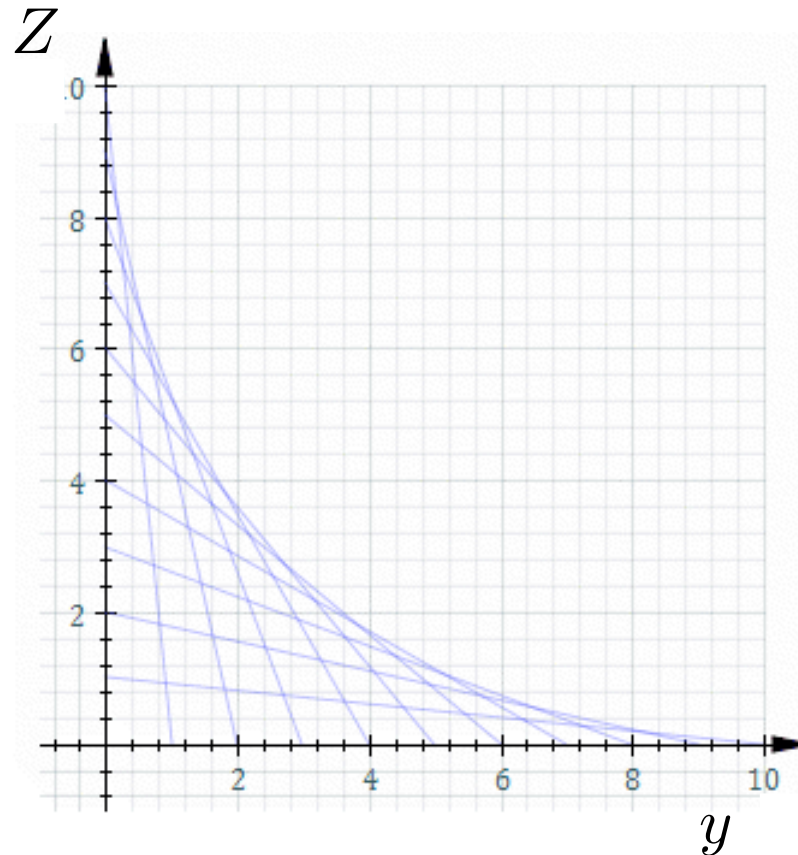
$$\frac{\partial N}{\partial x} = X, \quad \frac{\partial N}{\partial y} = -Y$$

# THE LEGENDRE TRANSFORMATION III

Curve in a plane can be equally represented by:

pairs of coordinates (point geometry)

envelope of a family of tangent lines (line geometry)



## THE LEGENDRE TRANSFORMATION IV

For given  $Z = Z(y)$  consider tangent line that goes through point  $(y, Z)$   
and has slope  $dZ/dy = Y$

If  $Z$  intercept is  $N$   $\rightarrow$  equation of line is given by (D)

$$Y = \frac{Z - N}{y - 0} \Rightarrow N = Z - yY$$

it follows that  $\rightarrow dN = dZ - ydY - Ydy$

but  $\rightarrow dZ = Ydy \Rightarrow dN = -y dY$

which is reciprocal relation  $\rightarrow y = -\frac{dN}{dY}$

Legendre transformation is mapping from  $(y, Z)$  space to  $(Y, N)$  space  
 $\rightarrow$  point representation of curve into tangent line representation

# ENTHALPY

Suppose we spontaneously create system while it is thermally insulated but in constant mechanical contact with "volume bath" @ pressure  $P$

$$W = U + PV$$

quantity  $U + PV$  → enthalpy

Legendre transformation with respect to pairs of variables  $P, V$

$$H = U + PV \quad (123)$$

so that in equilibrium →  $dH = dU + PdV + VdP$

Enthalpy should be considered as a function of  $S$  and  $P$

that are its **native variables** →  $dH = TdS + VdP \quad (124)$

It follows that →  $T = \left( \frac{\partial H}{\partial S} \right)_P$  and  $V = \left( \frac{\partial H}{\partial P} \right)_S \quad (125)$

and Maxwell relation →  $\left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P \quad (126)$



## ENTHALPY II

In general we have  $\Rightarrow dH \leq TdS + VdP$

In systems @ fixed  $(S, P)$

spontaneous processes drive enthalpy  $H$  to a minimum

For general systems

$$dH \leq TdS - \delta W + PdV + VdP$$

$$\delta W_{\text{free}} \leq TdS + VdP - dH$$

CONCLUSION: for systems @ fixed  $(S, P)$   $\Rightarrow \delta W_{\text{free}} \leq -dH$

## HELMHOLTZ FREE ENERGY

Suppose  $\rightarrow$  we spontaneously create system while it is in contact with thermal reservoir at temperature  $T$

$$\mathcal{W} = U - TS$$

quantity  $U - TS$   $\rightarrow$  Helmholtz free energy

Legendre transformation with respect to pairs of variables  $T, S$

$$F = U - TS \quad (127)$$

so that in equilibrium  $\rightarrow$   $dF = dU - TdS - SdT$

$F$  should be considered as a function of  $T$  and  $V$

that are its **native variables**  $\rightarrow$   $dF = -SdT - PdV$  (128)

It follows that  $\rightarrow$   $-S = \left(\frac{\partial F}{\partial T}\right)_V$  and  $-P = \left(\frac{\partial F}{\partial V}\right)_T$  (129)

and Maxwell relation  $\rightarrow$   $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$  (130)

## HELMHOLTZ FREE ENERGY II

In general the Second Law tells us  $\Rightarrow dF \leq -SdT - PdV$

Equality holds for reversible processes

and inequality for spontaneous processes

In systems @ fixed  $(T, V)$

spontaneous processes drive Helmholtz free energy  $F$  to a minimum

We may also write

work done by a thermodynamic system under conditions of constant  $T$

is bounded above by  $-dF$

and maximum  $\delta W$  is achieved for reversible processes

$$\delta W_{\text{free}} \leq -SdT - PdV - dF$$

CONCLUSION: for systems @ fixed  $(T, V)$   $\Rightarrow \delta W_{\text{free}} \leq -dF$

## GIBBS FREE ENERGY

If we create thermodynamic system at conditions of constant  $T$   
it absorbs heat energy  $Q = TS$  from reservoir  
and we must expend work energy  $PV$  in order to make room for it

$$W = U - TS + PV$$

Gibbs free energy is obtained by a second Legendre transformation

$$G = U - TS + PV \quad (131)$$

For equilibrium systems

$$dG = -SdT + VdP \quad (132)$$

so that  $G = G(T, P)$  in native variables

It follows that  $\Rightarrow$  
$$-S = \left( \frac{\partial G}{\partial T} \right)_P \quad \text{and} \quad V = \left( \frac{\partial G}{\partial P} \right)_T \quad (133)$$

and Maxwell relation  $\Rightarrow$  
$$-\left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial V}{\partial T} \right)_P \quad (134)$$

## GIBBS FREE ENERGY II

Second Law says that

$$dG \leq -SdT + VdP$$

In systems @ fixed  $(T, P)$

spontaneous processes drive Gibbs free energy  $G$  to a minimum

For general systems

$$\delta W_{\text{free}} \leq -SdT + VdP - dG$$

CONCLUSION: for systems @ fixed  $(T, P)$   $\rightarrow \delta W_{\text{free}} \leq -dG$

# HOMWORK ON THERMODYNAMIC POTENTIALS

For given  $F$  obtain:

entropy from (129)

$$\text{internal energy } U = F + TS = F - T \left( \frac{\partial F}{\partial T} \right)_V \quad (135)$$

$$\text{heat capacity } C_V = T \left( \frac{\partial S}{\partial T} \right)_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V \quad (136)$$

Show that for perfect gas combination of (58), (127), (115) yields

$$F = C_V T + U_0 - C_V T \ln(TV^{\gamma-1}) - TS_0 \quad (137)$$

Check that (135) and (136) yield familiar results for perfect gas

From (129) with the use of (50) obtain equation of state

$$P = - \left( \frac{\partial F}{\partial V} \right)_T = \frac{C_V T (\gamma - 1)}{V} = \frac{nRT}{V} \quad (138)$$

# OPEN SYSTEMS

Mass of system was considered as constant  
and dropped from arguments of thermodynamic functions

If system can exchange mass with environment  
or there are chemical reactions in system  
masses of components change and can cause change of other quantities

If mass is added to system with a constant volume  
pressure typically increases

Throughout we will consider number of particles  $N$   
instead of mass or number of kilomoles  $n$

Connection between  $N$  and  $n$  has been given in (6)

Using  $N$  is preferable in statistical physics  
while  $n$  is more convenient in chemistry

# CHEMICAL POTENTIAL

With account of mass changes  $\rightarrow$  internal energy becomes

$$U = U(S, V, N)$$

and main thermodynamic identity (84) should be modified accordingly

$$dU = TdS - PdV + \mu dN \quad (139)$$

chemical potential per particle  $\rightarrow \mu = \left( \frac{\partial U}{\partial N} \right)_{S,V} \quad (140)$

Chemical potential per kilomole  $\rightarrow$  substitute last term in (139) by  $\mu dn$

For multicomponent system such as mixture of different gases

described by numbers of particles  $N_i \rightarrow \mu dN \Rightarrow \sum_i \mu_i dN_i$



## EULER'S THEOREM

Since all arguments in  $U(S, V, N)$  are extensive quantities  
multiplying them all by a parameter  $\lambda$

means simply increasing whole system by  $\lambda$

that leads to increase of  $U$  by  $\lambda$

Mathematically  $\Rightarrow$  for any function  $f$  this property can be expressed as

$$\lambda f(x, y, z) = f(\lambda x, \lambda y, \lambda z) \quad (141)$$

Differentiate (141) with respect to  $\lambda$  and then set  $\lambda = 1$  to obtain

$$f = x \frac{\partial f}{\partial x} + y \frac{\partial f}{\partial y} + z \frac{\partial f}{\partial z} \quad (142)$$

Applying Euler's theorem

$$U = S \left( \frac{\partial U}{\partial S} \right)_{V, n_i} + V \left( \frac{\partial U}{\partial V} \right)_{S, n_i} + \sum_{j=1}^m n_j \left( \frac{\partial U}{\partial n_j} \right)_{S, V, n_i}$$

From the differential of  $U$ :

$$\left( \frac{\partial U}{\partial S} \right)_{V, n_i} = T, \quad \left( \frac{\partial U}{\partial V} \right)_{S, n_i} = -P, \quad \left( \frac{\partial U}{\partial n_j} \right)_{S, V, n_i} = \mu_j$$

## GIBBS-DUHEM RELATION

So that one obtains  $\Rightarrow U = TS - PV + \mu N$  (143)

Using definition of Gibbs free energy (131)

we rewrite this relation in the form  $\Rightarrow G = \mu N$  (144)

Chemical potential is Gibbs free energy per particle

For open systems  $\Rightarrow$  differentials of thermodynamic potentials become:  
(124), (128), (132)

$$dH = TdS + VdP + \mu dN \quad (145)$$

$$dF = -SdT - PdV + \mu dN \quad (146)$$

$$dG = -SdT + VdP + \mu dN \quad (147)$$

From (144) follows  $\Rightarrow dG = \mu dN + Nd\mu$  (148)

which combined with (147) yields the Gibbs-Duhem equation

$$SdT - VdP + Nd\mu = 0 \quad (149)$$

# GRAND POTENTIAL

Grand potential (a.k.a. Landau free energy) is defined by

$$\Omega = -PV = F - G \quad (150)$$

expressed in terms of  $(T, V, \mu)$  as native variables

Substitute (146) and (148) into (150) and differentiate to obtain

$$d\Omega = -SdT - PdV - Nd\mu \quad (151)$$

and

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} \quad P = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} \quad N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} \quad (152)$$

Second Law tells us  $\Rightarrow d\Omega \leq -\delta W - SdT - \mu dN - Nd\mu$

hence  $\Rightarrow \delta\widetilde{W}_{\text{free}} \equiv \delta W_{\text{free}} + \mu dN \leq -SdT - PdV - Nd\mu - d\Omega$

CONCLUSION: for systems @ fixed  $(T, V, \mu) \Rightarrow \delta\widetilde{W}_{\text{free}} \leq -d\Omega$

## APPLICATIONS

For given  $\Omega$   $\rightarrow$  other thermodynamic potentials can be obtained from it

$$G = -\mu \left( \frac{\partial \Omega}{\partial \mu} \right)_{T,V} \quad (153)$$

From (150) it follows that

$$F = \Omega - \mu \left( \frac{\partial \Omega}{\partial \mu} \right)_{T,V} \quad (154)$$

From  $\rightarrow U = F + TS$  it follows that

$$U = \Omega - \mu \left( \frac{\partial \Omega}{\partial \mu} \right)_{T,V} - T \left( \frac{\partial \Omega}{\partial T} \right)_{V,\mu} \quad (155)$$

From  $\rightarrow H = U + PV = U - \Omega$  it follows that

$$H = -\mu \left( \frac{\partial \Omega}{\partial \mu} \right)_{T,V} - T \left( \frac{\partial \Omega}{\partial T} \right)_{V,\mu} \quad (156)$$