Physical Chemistry for Energy Engineering

(12th: 2018/10/22)

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*The class follows the text book: D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

Course schedule (tentative)

Lecture #	Date	Contents
1	3-Sep	Introduction
2	5-Sep	1. Thermodynamics: Basic concepts of thermodynamics
3	10-Sep	1. Thermodynamics: The first law of thermodynamics
4	12-Sep	1. Thermodynamics: Thermodynamic process and cycle
5	17-Sep	1. Thermodynamics: The second and third laws of thermodynamics-1
6	19-Sep	1. Thermodynamics: The second and third laws of thermodynamics-2
	24-Sep	No lecture (holiday)
	26-Sep	No lecture (holiday)
7	1-Oct	1. Thermodynamics: The second and third laws of thermodynamics-3 (1. Equation of state of gas will be covered in future)
	3-Oct	No lecture (holiday)
8	8-Oct	Answer of homework-1
9	10-Oct	Exam-01 (2 hour)
10	15-Oct	2. Introduction to equilibrium theory
11	17-Oct	2. Free energy-1
12	22-Oct	2. Free energy-2
13	24-Oct	2. Calculation of thermodynamic quantities
	29-Oct	No lecture
	31-Oct	

Contents of today

<Last class>

- 2.2. Equilibrium theory: free energy
  - 2.2.1. Helmholtz energy
  - 2.2.2. Gibbs energy

<Today's class>

- 2.2. Equilibrium theory: free energy
  - **2.2.2. Gibbs energy**
  - 2.2.3. Maxwell relations and some useful formula
  - 2.2.4. How to calculate thermodynamic quantities

Review of the last class, equilibrium theory

Free energy as well as entropy is a good index to predict the equilibrium state and the direction of reaction.

- ✓ For an isolated system

  → Maximize the entropy: S

- ✓ For a system of constant T and constant V

  → Minimize the Helmholtz (free) energy: A

  $$A = U - TS$$

- ✓ For a system of constant T and constant P

  → Minimize the Gibbs (free) energy: G

  $$G = H - TS = A + PV$$

2.2.2. Gibbs energy
- examples for how to determine the reaction direction-

(Example-2) A vaporization “H_2O (l) → H_2O (g)”

- ✓ The molar Gibbs energy of vaporization ($\Delta_{vap}\bar{G}$) is:

$$\Delta_{vap}\bar{G} = \bar{G}[H_2O(g)] - \bar{G}[H_2O(l)] = \Delta_{vap}\bar{H} - T\Delta_{vap}\bar{S}$$

- ✓ $\Delta_{vap}\bar{H} = 40.65\ kJ\ mol^{-1}$ and $\Delta_{vap}\bar{S} = 108.9\ J\ K^{-1}\ mol^{-1}$ at 1 bar (1x10^5 Pa) near 373.15 K (100ºC). Thus,

$$\Delta_{vap}\bar{G} = 40.65 - T \times 0.1089\ \ \mathrm{k}J\ mol^{-1}$$

  - ➢ If $\mathrm{T} = 373.15\ K$,

$$\Delta_{vap}\bar{G} = \cdots$$

  - ➢ If $\mathrm{T} = 363\ K$ (slightly lower than the normal melting point),

$$\Delta_{vap}\bar{G} = \cdots$$

  - ➢ If $\mathrm{T} = 383\ K$ (slightly higher than the normal melting point),

$$\Delta_{vap}\bar{G} = \cdots$$

2.2.2. Gibbs energy
- examples for how to determine the reaction direction-

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$$\Delta_{vap}\bar{G} = 40.65 - T \times 0.1089\ \ \mathrm{kJ}\ mol^{-1}$$

  - ➢ If $\mathrm{T} = 373.15\ K$,

$$\Delta_{vap}\bar{G} = 40.65 - 373.15 \times 108.9 = 0\ kJ\ mol^{-1}$$

    which means the transfer of 1 mole liquid water to water vapor is a reversible process at 373.15 K at 1x10^5 Pa.

  - ➢ If $\mathrm{T} = 363\ K$ (slightly lower than the normal melting point),

$$\Delta_{vap}\bar{G} = 40.65 - 363.15 \times 0.1089 = +1.12\ kJ\ mol^{-1}$$

    which means the water vaporization is not spontaneous at 363 K at 1x10^5 Pa.

  - ➢ If $\mathrm{T} = 383\ K$ (slightly higher than the normal melting point),

$$\Delta_{vap}\bar{G} = 40.65 - 383.15 \times 0.1089 = -1.06\ kJ\ mol^{-1}$$

    which means the vaporization is spontaneous at 383 K at 1x10^5 Pa.

2.2.2. Gibbs energy

- examples for how to determine the work to be obtained/required-

(Example-3: a case of "$\Delta G < 0$") Combustion of H_2

H_2 (g) + ½ O_2 (g)$\rightarrow$ H_2O (l)   @298.15 K and 1 bar ($1\text{x}10^5$ Pa)

- ✓ $\Delta_r G = -237.1\ kJ\ mol^{-1}$ at 298.15 K and $1\text{x}10^5$ Pa.
- ✓ Thus, a maximum of -237.1 kJ mol^{-1} of usual work (excluding reversible P-V work) can be obtained from this spontaneous reaction.
- ✓ If some energies are irreversibly transferred and thus causing temperature increase (e.g. friction), we cannot reconvert some of it to "usual work", due to the second law.

(Example-4: a case of "$\Delta G > 0$") Decomposition of H_2O

H_2O (l) $\rightarrow$ H_2 (g) + ½ O_2 (g) @298.15 K and 1 bar ($1\text{x}10^5$ Pa)

- ✓ As the opposite reaction of H_2 combustion, $\Delta_r G = 237.1\ kJ\ mol^{-1}$ at 298.15 K and $1\text{x}10^5$ Pa.
- ✓ Thus, it would require at least 237.1 kJ mol^{-1} of energy to drive this (nonspontaneous) reaction.
- ✓ If some non-reversible processes are involved (certainly involved in practice), some additional energy to 237.1 kJ mol^{-1} have to be put on the system.

2.2.2. Gibbs energy
- examples for how to determine the work to be obtained/required-

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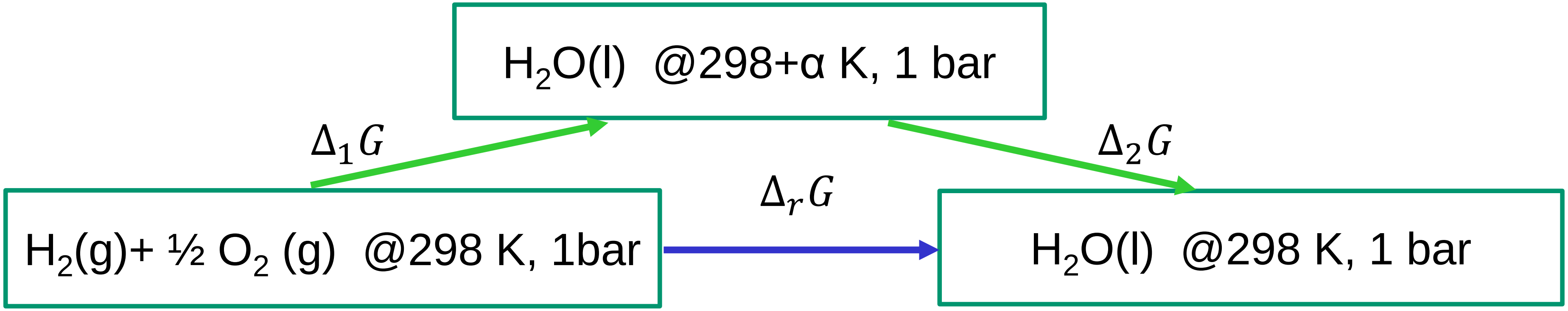

H_2O(l) @298+α K, 1 bar

$\Delta_1 G$

$\Delta_2 G$

$\Delta_r G$

H_2(g)+ ½ O_2 (g) @298 K, 1bar

H_2O(l) @298 K, 1 bar

- ✓ As the Gibbs energy is a state function, $\Delta_r G = \Delta_1 G + \Delta_2 G$
- ✓ We cannot take $\Delta_r G$ work from this reaction, because some irreversible processes should be involved.
  - ✓ Combustion explosively occurs in general, which is far away from reversible process where process should go slowly and the system is always at some equilibrium state.

2.2.2. Gibbs energy

- examples for how to determine the work to be obtained/required-

(Example-1: a case of "$\Delta G < 0$“) Combustion of H_2

H_2 (g) + ½ O_2 (g)→ H_2O (l) @298.15 K and 1 bar (1x10^5 Pa)

- ✓ $\Delta_r G = -237.1\ kJ\ mol^{-1}$ at 298.15 K and 1x10^5 Pa.

- ✓ We may take some electrical energy out of the chemical energy by
  - ➢ [(2) directly to electrical energy] using a fuel cell.

    “H_2 → $2H^+ + 2e^-$ “ (anode) & “$2H^+$ + ½ O_2 + $2e^-$ → H_2O (cathode)

    *theoretical efficiency = $\Delta G/\Delta H$ = $(\Delta H - T\Delta S)/\Delta H$

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- 2.2. Equilibrium theory: free energy
  - 2.2.2. Gibbs energy
  - **2.2.3. Maxwell relations and some useful formula**
  - 2.2.4. How to calculate thermodynamic quantities

2.2.3. Maxwell relations and some useful formulas
- Maxwell relations for Helmholtz energy ($22.2)-

As an example, a “Maxwell relation” for Helmholtz energy (A) is given here.

Differential equation of Helmholtz energy ($\mathrm{A} = U - TS$) is:

$$dA = dU - TdS - SdT$$

Considering a process along a reversible path, the first and second laws are:

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$

Hence,

$$dA = -PdV - SdT$$

Here, we can compare it with the total differential of $\mathrm{A} = A(V, T)$

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT \ , \quad \text{then}$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \ \text{ and } \left(\frac{\partial A}{\partial T}\right)_V = -S$$

Since, the cross derivatives are equal as:

$$\left(\frac{\partial^2 A}{\partial T \partial V}\right) = \left(\frac{\partial^2 A}{\partial V \partial T}\right) \ , \text{then}$$

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

(Appendix) cross derivatives -

We consider a case of F for “F is a function of x and y, namely $F = F(x, y)$”

$$\left(\frac{\partial^2 F}{\partial y \partial x}\right) = \frac{\partial}{\partial y}\left(\frac{\partial F}{\partial x}\right) = \frac{\partial}{\partial y}\left[\frac{F(x+\Delta x, y) - F(x, y)}{\Delta x}\right]$$

$$= \left\{\left[\frac{F(x+\Delta x, y+\Delta y) - F(x, y+\Delta y)}{\Delta x}\right] - \left[\frac{F(x+\Delta x, y) - F(x, y)}{\Delta x}\right]\right\}/\Delta y$$

$$= \left\{\left[\frac{F(x+\Delta x, y+\Delta y) - F(x+\Delta x, y)}{\Delta y}\right] - \left[\frac{F(x, y+\Delta y) - F(x, y)}{\Delta y}\right]\right\}/\Delta x$$

$$= \frac{\partial}{\partial x}\left[\frac{F(x, y+\Delta y) - F(x, y)}{\Delta y}\right] = \frac{\partial}{\partial x}\left(\frac{\partial F}{\partial y}\right) = \left(\frac{\partial^2 F}{\partial x \partial y}\right)$$

2.2.3. Maxwell relations and some useful formulas
- Maxwell relations for Helmholtz energy ($22.2)-

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

This kind of equation, which is obtained by the second cross partial derivatives of A (U, H, and G, as well) is called a Maxwell relation.

Indeed, Maxwell relation give us a useful equations.
For example, here, we assume a constant temperature process, then:

$$\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T}\right)_V dV \qquad \text{(constant T)}$$

- If we know a P-V-T data, such as the equation of state, this is easily utilized to determine *S*.
  - For an ideal gas, for example,

$$\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial}{\partial T}\left(\frac{nRT}{V}\right)\right)_V dV = nR\int_{V_1}^{V_2} \frac{dV}{V} = nR\ln\frac{V_2}{V_1}$$

(*constant T)

- If V_1 is very large, a gas behaves as an ideal gas. So, we can evaluate ΔS in reference to $S^{ideal\text{-}gas}$ value.

2.2.3. Maxwell relations and some useful formulas
- Maxwell relations for Gibbs energy ($22.2)-

Here, we consider the Maxwell relation for Gibbs energy (G).

Differential equation of Gibbs energy ($G = U - TS + PV$) is:

$$dG = dU - TdS - SdT + PdV + VdP$$

Considering a process along a reversible path, the first and second laws are:

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$

Hence,

$$dG = -SdT + VdP$$

Here, we can compare it with the total derivative of $G = G(T, P)$

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \quad , \quad \text{then}$$

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

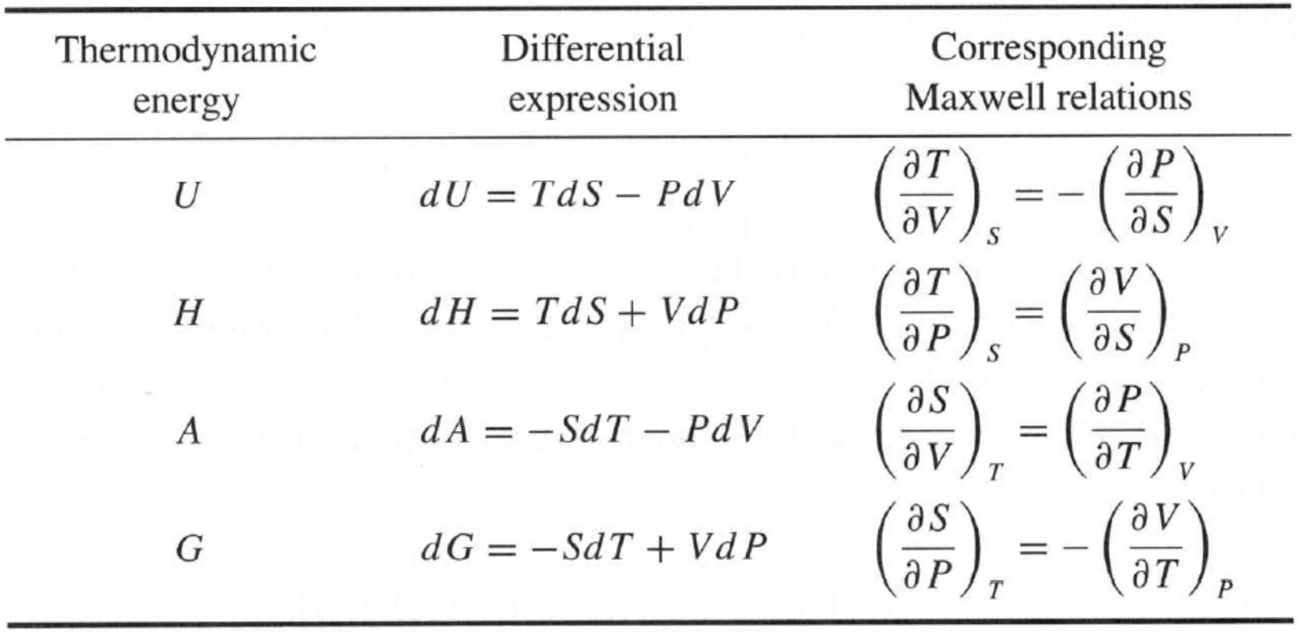
Since, the cross derivatives are equal as:

$$\left(\frac{\partial^2 G}{\partial T \partial P}\right) = \left(\frac{\partial^2 G}{\partial P \partial T}\right) \quad \text{, then}$$

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

2.2.3. Maxwell relations and some useful formulas
- Maxwell relations ($22.2)-

- Likewise, the four principal thermodynamic energies (*U, H, A, G*), have natural independent variables and then Maxwell relations as follows.
- These differential expression were derived only according to the first & second laws and considering a reversible path.
    - Even for non-equilibrium states and/or for irreversible processes, as far as thermodynamic quantities are definitely determined at around the concerned state, these relations are applicable because they are about state functions.



Thermodynamic energy	Differential expression	Corresponding Maxwell relations
U	$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
H	$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
A	$dA = -SdT - PdV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
G	$dG = -SdT + VdP$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

*D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

2.2.3. Maxwell relations and some useful formulas
- Maxwell relations for Gibbs energy ($22.2)-

The meaning of “natural independent variables” is given for U as example.

Considering a process along a reversible path, the first and second laws are:

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$

Here, the variables of U are S and V.

However, if we wish, we can use T and V as the variables of U, for example:

$$dU = \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV + C_V dT$$

In comparison,

$$dU = TdS - PdV$$

is apparently more simple. Thus we consider S and V are “natural independent variables” for U.

2.2.3. Maxwell relations and some useful formulas
- some useful formulas from Maxwell relations ($22.7)-

Similarly, we can derive several useful equations.

(1) A equation which plays a central role in chemical equilibria involving gas-phase reactions.

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \text{then} \qquad \Delta G = \int_{P_1}^{P_2} V dP \qquad \text{(constant T)}$$

For 1 mole of an ideal gas (constant T),

$$\Delta \bar{G} = RT \int_{P_1}^{P_2} \frac{dP}{P} = RT \ln \frac{P_2}{P_1}$$

$$\bar{G} = G°(T) + RT \ln\left(\frac{P}{1\ bar}\right)$$

Here, $G°(T)$ is called the standard molar Gibbs energy.
It is the Gibbs energy of 1 mole of the ideal gas at a pressure of 1 bar at T K, which is called “standard state”.

*1 bar = 1x10^5 Pa

2.2.3. Maxwell relations and some useful formulas
- some useful formulas from Maxwell relations ($22.7)--

Similarly, we can derive several useful equations.

(2) A equation (called Gibbs-Helmholtz equation) which is used to derive an equation for the temperature dependence of an equilibrium constant.

$G = H - TS$ then $\frac{G}{T} = \frac{H}{T} - S$

By differentiating partially with respect to T keeping P fixed:

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2} + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P$$

As $C_P(T) = (\partial H/\partial T)_P = T(\partial S/\partial T)_P$,

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2}$$

This equation can be directly applied to any process, in which case it is:

$$\left(\frac{\partial \Delta G/T}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$$

Legendre transformation and application

Legendre transformation is the transformation from *f(x)* to *g(p)* as follows:

$$g^*(p) = \max_x \{ px - f(x) \}$$

where x is taken so that $\{px-f(x)\}$ is maximized.
(*If the maximum does not exist, "max" is replaced with "sup".)
The inverse transformation is given as

$$f^{**}(x) = -\min_p \{ f^*(p) - xp \}$$

This corresponds to do the transformation twice. For a convex function, $f^{**}(x)$ is equal to $f(x)$.

(Exercise) Do the Legendre transformation for $f(x) = ax^2$, where $a > 0$. And then, do the inverse transformation.

Legendre transformation and application

$$g^*(p) = \max_x \{px - f(x)\} \qquad f^{**}(x) = -\min_p \{g^*(p) - xp\}$$

(Exercise) Do the Legendre transformation for $f(x) = ax^2$, where $a > 0$. And then, do the inverse transformation.

$$g^*(p) = \max_x \{px - ax^2\}$$

$$= \max_x \left\{ -a\left(x - \frac{p}{2a}\right)^2 + \frac{p^2}{4a} \right\} = \frac{p^2}{4a}$$

$$f^{**}(x) = -\min_p \{g^*(p) - xp\}$$

$$= -\min_p \left\{ \frac{p^2}{4a} - xp \right\} = -\min_p \left\{ \frac{(p - 2ax)^2}{4a} - ax^2 \right\}$$

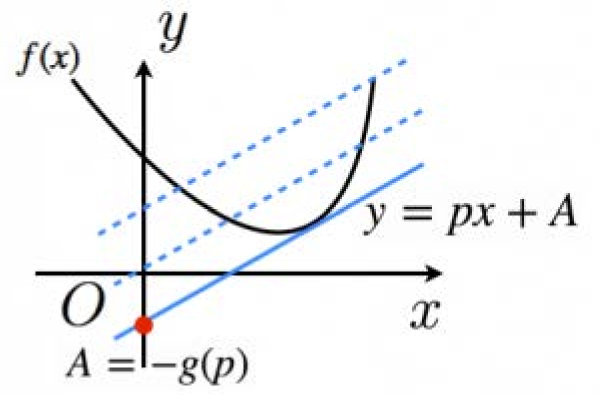
$$= ax^2$$

$$px - ax^2 = -A$$

$$px + A = ax^2$$

We minimize A here.

Then, $g(p) = -A$



https://mathtrain.jp/legendrehenkan

Legendre transformation and application

For a function whose independent variables are *x* and *y*, namely $\phi(x,y)$, if it is (total) differentiable,

$$\phi(x,y) = \left(\frac{\partial \phi}{\partial x}\right)_y dx + \left(\frac{\partial \phi}{\partial y}\right)_x dy = udx + vdy$$

$$\text{where} \quad u \equiv \left(\frac{\partial \phi}{\partial x}\right)_y , \quad v \equiv \left(\frac{\partial \phi}{\partial y}\right)_x$$

Now, we want to find an equation that regards u and v are independent variables. First, to convert the variable $x \rightarrow u$, we define ψ as

$$\psi \equiv \phi - xu \qquad \longleftarrow \quad \text{This is Legendre transformation}$$

then

$$d\psi = d\phi - d(xu) = (udx + vdy) - (xdu + udx) = -xdu + vdy$$

Legendre transformation and application

$$\phi(x,y)=\left(\frac{\partial\phi}{\partial x}\right)_y dx+\left(\frac{\partial\phi}{\partial y}\right)_x dy=udx+vdy$$

where $u\equiv\left(\frac{\partial\phi}{\partial x}\right)_y$, $v\equiv\left(\frac{\partial\phi}{\partial y}\right)_x$

$$d\psi=d\phi-d(xu)=(udx+vdy)-(xdu+udx)=-xdu+vdy$$

Comparing this with $d\psi=\left(\frac{\partial\psi}{\partial u}\right)_y du+\left(\frac{\partial\psi}{\partial y}\right)_u dy$ gives us the following relations

$$\boxed{-x=\left(\frac{\partial\psi}{\partial u}\right)_y ,v=\left(\frac{\partial\psi}{\partial y}\right)_u .}$$

(Exercise) For $\phi(x,y)$, convert the variable $y\longrightarrow v$,

Legendre transformation and application

$$\phi(x,y)=\left(\frac{\partial\phi}{\partial x}\right)_y dx+\left(\frac{\partial\phi}{\partial y}\right)_x dy=udx+vdy,\quad \text{where}\quad u\equiv\left(\frac{\partial\phi}{\partial x}\right)_y,\quad v\equiv\left(\frac{\partial\phi}{\partial y}\right)_x$$

$$d\psi=d\phi-d(xu)=(udx+vdy)-(xdu+udx)=-xdu+vdy$$

Comparing this with $d\psi=\left(\frac{\partial\psi}{\partial u}\right)_y du+\left(\frac{\partial\psi}{\partial y}\right)_u dy$ gives us the following relations

$$-x=\left(\frac{\partial\psi}{\partial u}\right)_y, v=\left(\frac{\partial\psi}{\partial y}\right)_u .$$

(Exercise) For $\phi(x,y)$, convert the variable $y\to v$,

Legendre transformation and application

$$\boxed{\phi(x,y)=\left(\frac{\partial\phi}{\partial x}\right)_y dx+\left(\frac{\partial\phi}{\partial y}\right)_x dy=udx+vdy,\quad \text{where}\quad u\equiv\left(\frac{\partial\phi}{\partial x}\right)_y,\quad v\equiv\left(\frac{\partial\phi}{\partial y}\right)_x}$$

To convert the variable $y \rightarrow v$, we define as

$$\lambda\equiv\phi-yv$$

$$d\lambda=d\phi-d(yv)=(udx+vdy)-(ydv+vdy)=udx-ydv$$

Comparing this with relations $d\lambda=\left(\frac{\partial\lambda}{\partial x}\right)_v dx+\left(\frac{\partial\lambda}{\partial v}\right)_x dv$ gives us the following

$$\boxed{u=\left(\frac{\partial\lambda}{\partial x}\right)_v,-y=\left(\frac{\partial\lambda}{\partial v}\right)_x.}$$

Legendre transformation and application

$$\boxed{\phi(x,y)=\left(\frac{\partial\phi}{\partial x}\right)_y dx+\left(\frac{\partial\phi}{\partial y}\right)_x dy=udx+vdy,\quad \text{where}\quad u\equiv\left(\frac{\partial\phi}{\partial x}\right)_y,\quad v\equiv\left(\frac{\partial\phi}{\partial y}\right)_x}$$

Likewise, to have an equation where *u* and *v* are independent variables, starting from $\psi \equiv \phi - xu$, whose independent variables are *x* and *v*,

$$\mu \equiv \psi - yv$$

$$d\mu = d\psi - d(yv) = (-xdu + vdy) - (ydv + vdy) = -xdu - ydv$$

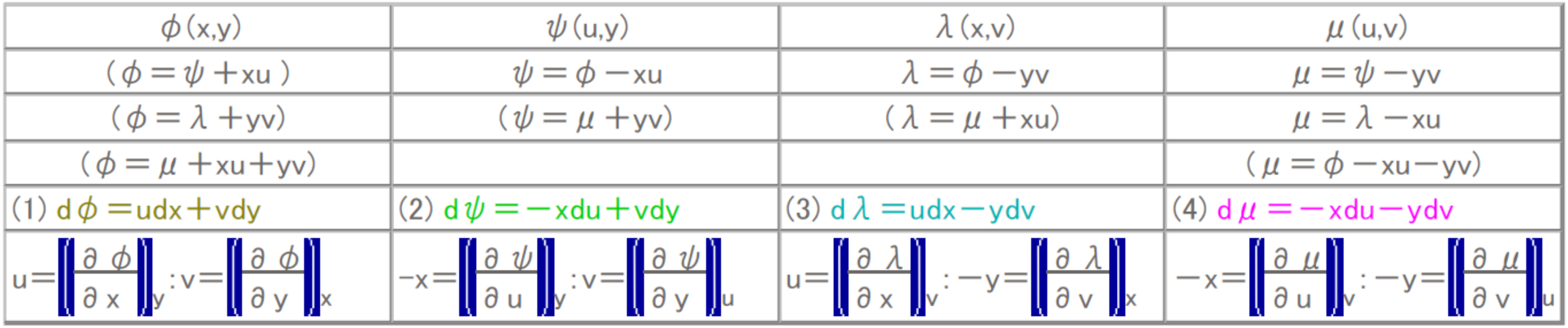
Comparing this with $d\mu = \left(\frac{\partial\mu}{\partial u}\right)_v du + \left(\frac{\partial\mu}{\partial v}\right)_u dv$ gives us the following relations

$$\boxed{-x=\left(\frac{\partial\mu}{\partial u}\right)_v,\ -y=\left(\frac{\partial\mu}{\partial v}\right)_u .}$$

Legendre transformation and application

$$\phi(x,y)=\left(\frac{\partial\phi}{\partial x}\right)_y dx+\left(\frac{\partial\phi}{\partial y}\right)_x dy=udx+vdy,\quad \text{where}\quad u\equiv\left(\frac{\partial\phi}{\partial x}\right)_y,\quad v\equiv\left(\frac{\partial\phi}{\partial y}\right)_x$$

In summary,



ϕ(x,y)	ψ(u,y)	λ(x,v)	μ(u,v)
($\phi=\psi+xu$)	$\psi=\phi-xu$	$\lambda=\phi-yv$	$\mu=\psi-yv$
($\phi=\lambda+yv$)	($\psi=\mu+yv$)	($\lambda=\mu+xu$)	$\mu=\lambda-xu$
($\phi=\mu+xu+yv$)			($\mu=\phi-xu-yv$)
(1) $d\phi=udx+vdy$	(2) $d\psi=-xdu+vdy$	(3) $d\lambda=udx-ydv$	(4) $d\mu=-xdu-ydv$
$u=\left(\frac{\partial\phi}{\partial x}\right)_y : v=\left(\frac{\partial\phi}{\partial y}\right)_x$	$-x=\left(\frac{\partial\psi}{\partial u}\right)_y : v=\left(\frac{\partial\psi}{\partial y}\right)_u$	$u=\left(\frac{\partial\lambda}{\partial x}\right)_v : -y=\left(\frac{\partial\lambda}{\partial v}\right)_x$	$-x=\left(\frac{\partial\mu}{\partial u}\right)_v : -y=\left(\frac{\partial\mu}{\partial v}\right)_u$

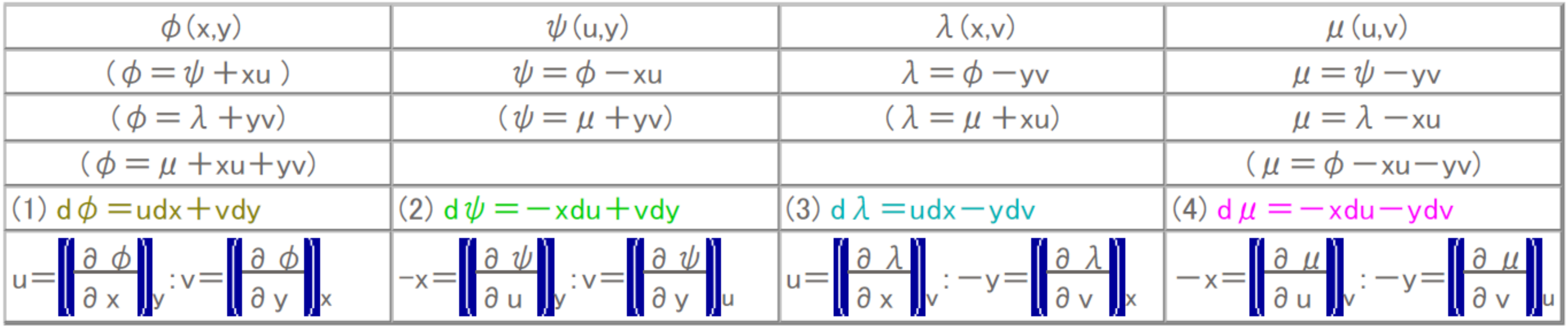
http://www.f-denshi.com/000TokiwaJPN/10kaisk/080ksk.html

(Exercise) Please relate ϕ, …, x, … with thermodynamic quantities, assuming $\phi=H$, $x=S$,

Legendre transformation and application

$$\phi(x,y)=\left(\frac{\partial\phi}{\partial x}\right)_y dx+\left(\frac{\partial\phi}{\partial y}\right)_x dy=udx+vdy,\quad \text{where}\quad u\equiv\left(\frac{\partial\phi}{\partial x}\right)_y,\quad v\equiv\left(\frac{\partial\phi}{\partial y}\right)_x$$

In summary,



$\phi(x,y)$	$\psi(u,y)$	$\lambda(x,v)$	$\mu(u,v)$
$(\phi=\psi+xu)$	$\psi=\phi-xu$	$\lambda=\phi-yv$	$\mu=\psi-yv$
$(\phi=\lambda+yv)$	$(\psi=\mu+yv)$	$(\lambda=\mu+xu)$	$\mu=\lambda-xu$
$(\phi=\mu+xu+yv)$			$(\mu=\phi-xu-yv)$
(1) $d\phi=udx+vdy$	(2) $d\psi=-xdu+vdy$	(3) $d\lambda=udx-ydv$	(4) $d\mu=-xdu-ydv$
$u=\left[\!\left[\frac{\partial\phi}{\partial x}\right]\!\right]_y : v=\left[\!\left[\frac{\partial\phi}{\partial y}\right]\!\right]_x$	$-x=\left[\!\left[\frac{\partial\psi}{\partial u}\right]\!\right]_y : v=\left[\!\left[\frac{\partial\psi}{\partial y}\right]\!\right]_u$	$u=\left[\!\left[\frac{\partial\lambda}{\partial x}\right]\!\right]_v : -y=\left[\!\left[\frac{\partial\lambda}{\partial v}\right]\!\right]_x$	$-x=\left[\!\left[\frac{\partial\mu}{\partial u}\right]\!\right]_v : -y=\left[\!\left[\frac{\partial\mu}{\partial v}\right]\!\right]_u$

http://www.f-denshi.com/000TokiwaJPN/10kaisk/080ksk.html

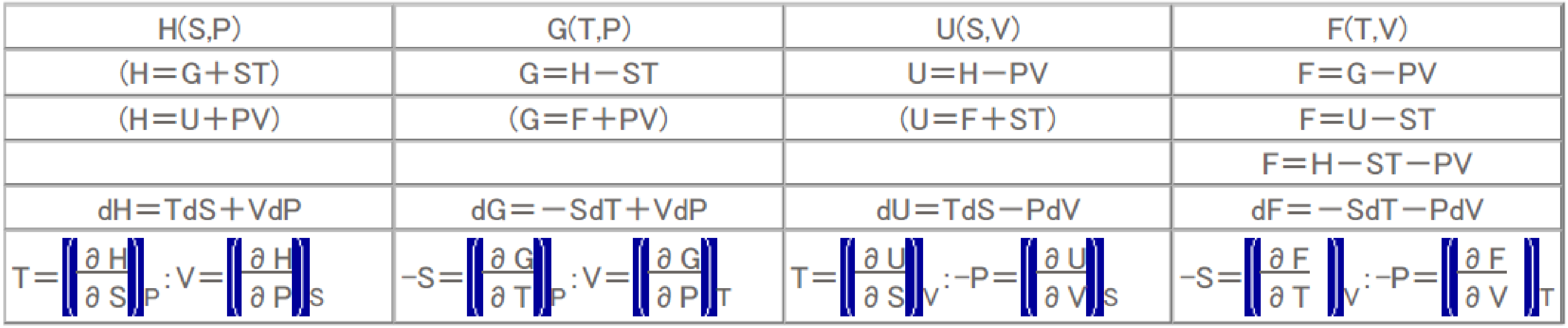
(Exercise) Please relate ϕ, …, x, … with thermodynamic quantities, assuming $\phi=H$, $x=S$,

$\phi=H$, $\psi=G$, $\lambda=U$, $\mu=F$,
$x=S$, $y=P$, $u=T$, $v=V$

Legendre transformation and application

$$\phi(x,y)=\left(\frac{\partial\phi}{\partial x}\right)_y dx+\left(\frac{\partial\phi}{\partial y}\right)_x dy=udx+vdy,\quad \text{where}\quad u\equiv\left(\frac{\partial\phi}{\partial x}\right)_y,\quad v\equiv\left(\frac{\partial\phi}{\partial y}\right)_x$$

In summary,



H(S,P)	G(T,P)	U(S,V)	F(T,V)
(H=G+ST)	G=H−ST	U=H−PV	F=G−PV
(H=U+PV)	(G=F+PV)	(U=F+ST)	F=U−ST
			F=H−ST−PV
dH=TdS+VdP	dG=−SdT+VdP	dU=TdS−PdV	dF=−SdT−PdV
$T=\left(\frac{\partial H}{\partial S}\right)_P : V=\left(\frac{\partial H}{\partial P}\right)_S$	$-S=\left(\frac{\partial G}{\partial T}\right)_P : V=\left(\frac{\partial G}{\partial P}\right)_T$	$T=\left(\frac{\partial U}{\partial S}\right)_V : -P=\left(\frac{\partial U}{\partial V}\right)_S$	$-S=\left(\frac{\partial F}{\partial T}\right)_V : -P=\left(\frac{\partial F}{\partial V}\right)_T$

http://www.f-denshi.com/000TokiwaJPN/10kaisk/080ksk.html

The relations in the last row become the Maxwell relations by using the fact “the cross derivatives are equal to each other”.

Contents of today

<Last class>

- 2.2. Equilibrium theory: free energy
  - 2.2.1. Helmholtz energy
  - 2.2.2. Gibbs energy

<Today's class>

- 2.2. Equilibrium theory: free energy
  - 2.2.2. Gibbs energy
  - 2.2.3. Maxwell relations and some useful formula
  - **2.2.4. How to calculate thermodynamic quantities**

2.2.4. How to calculate thermodynamic quantities
- standard state -

- We have a database of thermodynamic quantities. Because such quantities depend on conditions (temperature, pressure, etc), we use a specific condition, so-called "standard state".
  - For extensive quantities, molar quantity (quantity per mole) is used.
  - e.g. $\bar{S}^{\circ}$ where the bar stands for molar quantity and ° for the standard state.
- The standard state for each phase is defined as follows:
  - for a gas is the equivalent hypothetical ideal gas
  - for a liquid is the pure liquid substance
  - for a solid is the pure crystalline substance

at 1 bar at the temperature of interest.

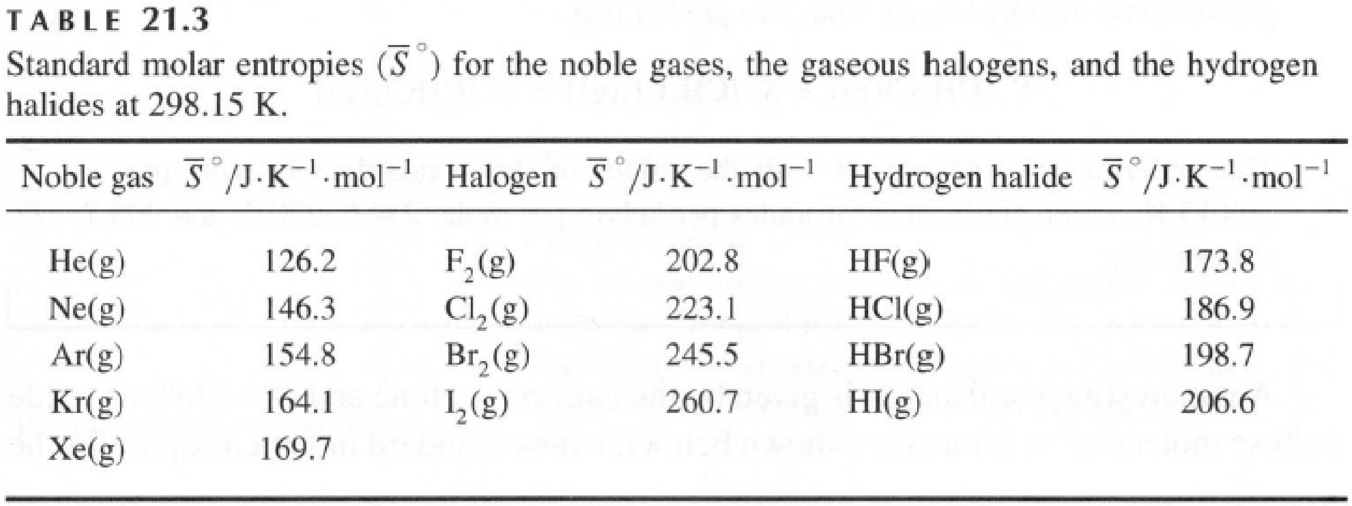


TABLE 21.3

Standard molar entropies ($\bar{S}^{\circ}$) for the noble gases, the gaseous halogens, and the hydrogen halides at 298.15 K.

Noble gas	$\bar{S}^{\circ}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	Halogen	$\bar{S}^{\circ}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	Hydrogen halide	$\bar{S}^{\circ}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$
He(g)	126.2	F_2(g)	202.8	HF(g)	173.8
Ne(g)	146.3	Cl_2(g)	223.1	HCl(g)	186.9
Ar(g)	154.8	Br_2(g)	245.5	HBr(g)	198.7
Kr(g)	164.1	I_2(g)	260.7	HI(g)	206.6
Xe(g)	169.7				

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

2.2.4. How to calculate thermodynamic quantities
- entropy calculation and “hypothetical ideal gas”($22-6) -

Using a equation based on the Maxwell relation for G, we can calculate the entropy at the temperature of interest.

The entropy change due to the temperature change of the substance is given as

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P(T')dT'}{T'}$$

(constant P)

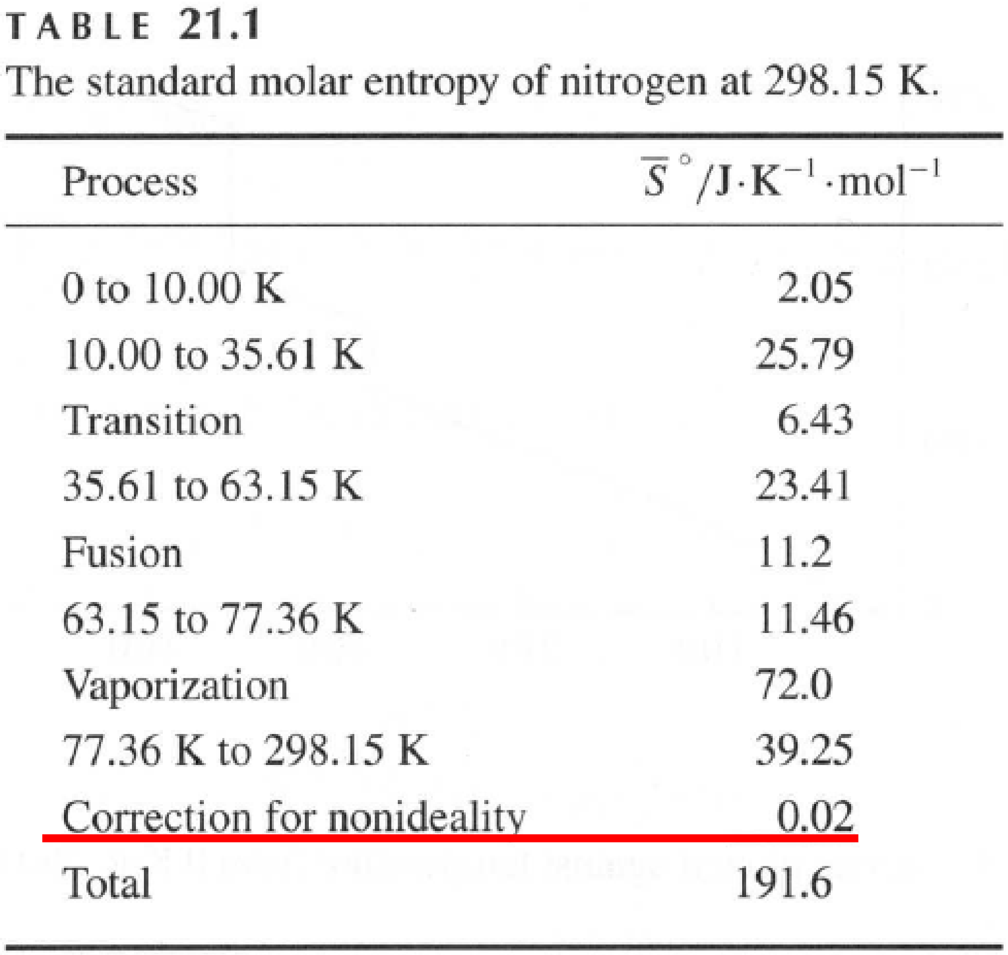


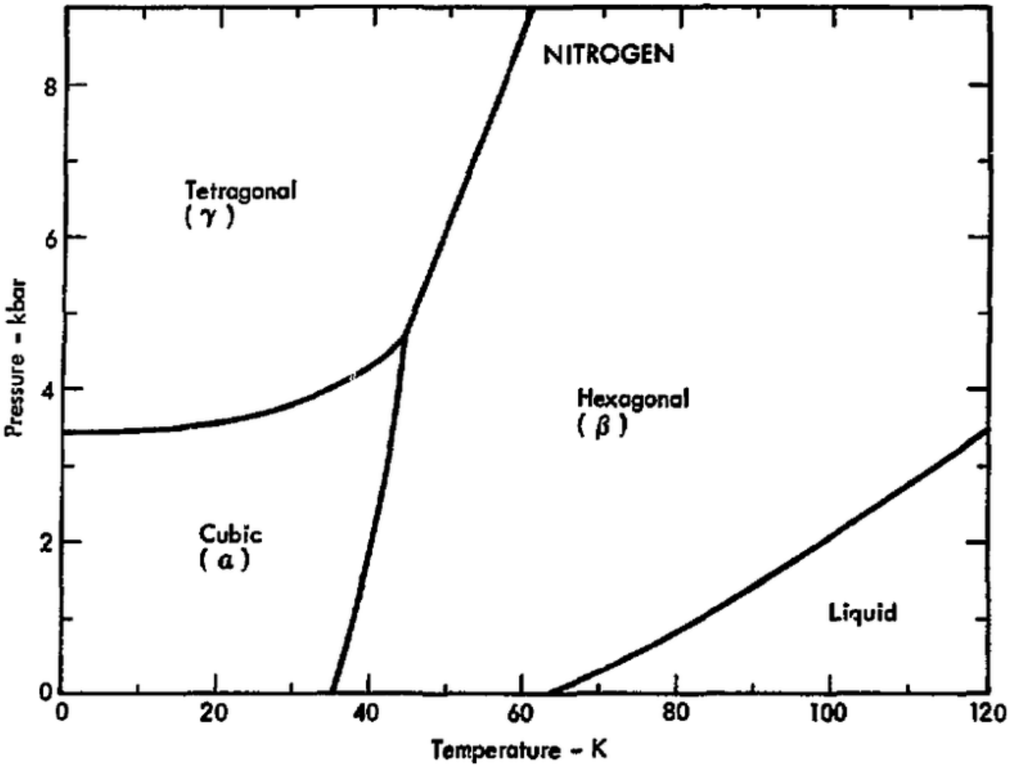
TABLE 21.1

The standard molar entropy of nitrogen at 298.15 K.

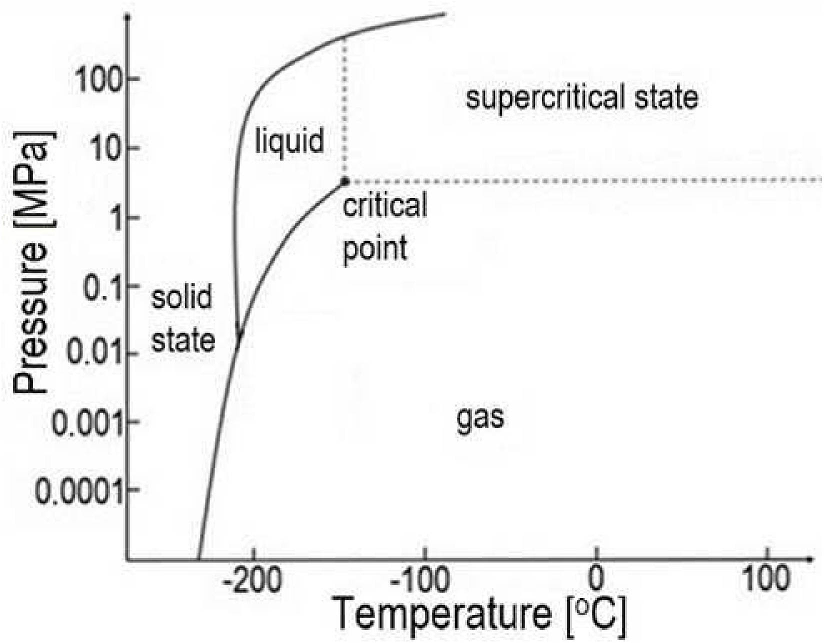
Process	$\overline{S}^\circ/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$
0 to 10.00 K	2.05
10.00 to 35.61 K	25.79
Transition	6.43
35.61 to 63.15 K	23.41
Fusion	11.2
63.15 to 77.36 K	11.46
Vaporization	72.0
77.36 K to 298.15 K	39.25
Correction for nonideality	0.02
Total	191.6

*D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

(Appendix) Phase diagram of nitrogen



https://commons.wikimedia.org/wiki/File:Phase_diagram_of_nitrogen_(1975).png



https://www.researchgate.net/publication/315888614_Selected_aspects_of_manufacturing_and_strength_evaluation_of_porous_composites_based_on_numerical_simulations/figures?lo=1