Physical Chemistry
for Energy Engineering
(13th: 2018/10/24)

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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

      2.2.2. Gibbs energy

      2.2.3. Maxwell relations and some useful formula

      2.2.4. How to calculate thermodynamic quantities

<Today's class>

    2.2. Equilibrium theory: free energy

    2.2.4. How to calculate thermodynamic quantities

✓ 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	$dU = TdS - PdV$	$\left(\dfrac{\partial T}{\partial V}\right)_S = -\left(\dfrac{\partial P}{\partial S}\right)_V$
H	$dH = TdS + VdP$	$\left(\dfrac{\partial T}{\partial P}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_P$
A	$dA = -SdT - PdV$	$\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$
G	$dG = -SdT + VdP$	$\left(\dfrac{\partial S}{\partial P}\right)_T = -\left(\dfrac{\partial V}{\partial T}\right)_P$

*textbook, Table 22.1

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

(Review) 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	$\bar{S}^{\circ}/J\cdot K^{-1}\cdot mol^{-1}$	Halogen	$\bar{S}^{\circ}/J\cdot K^{-1}\cdot mol^{-1}$	Hydrogen halide	$\bar{S}^{\circ}/J\cdot K^{-1}\cdot mol^{-1}$
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).

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)

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

TABLE 21.1

The standard molar entropy of nitrogen at 298.15 K.

Process	$\overline{S}^{\circ}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
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

(Review) (Appendix) Phase diagram of nitrogen
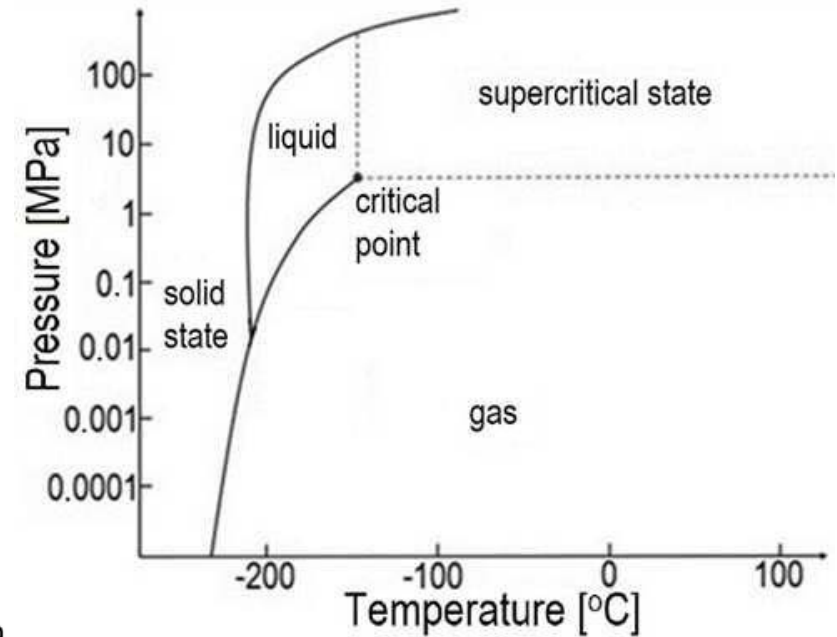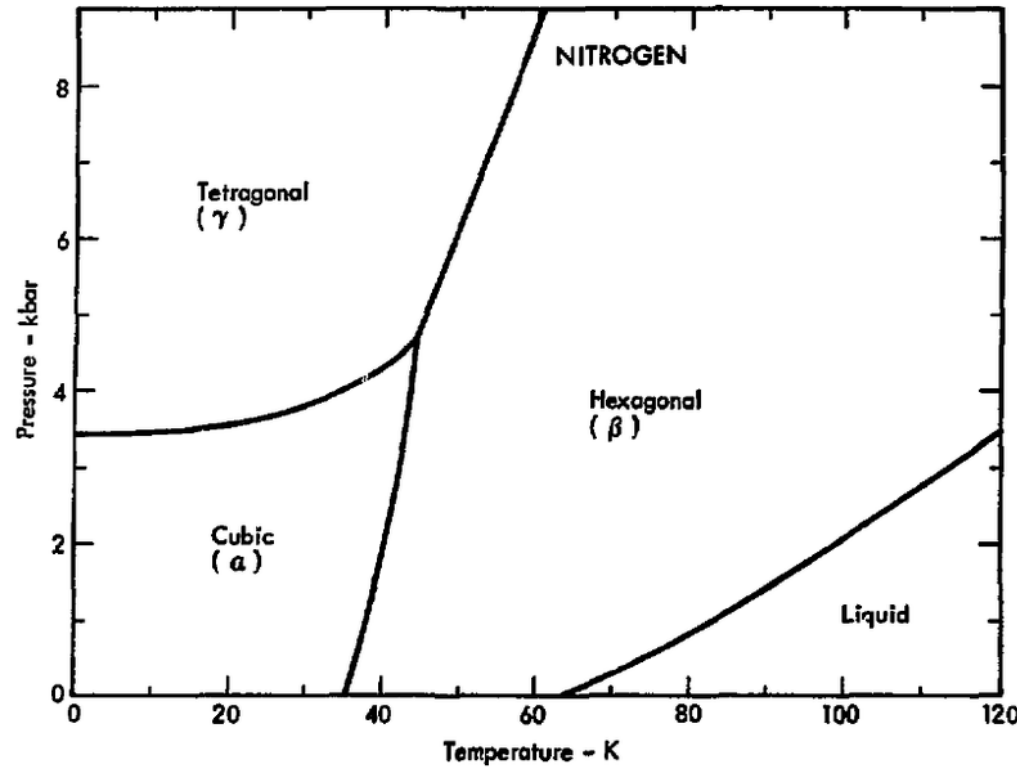
https://commons.wikimedia.org/wiki/File:
Phase_diagram_of_nitrogen_(1975).png

https://www.researchgate.net/publication/3
15888614_Selected_aspects_of_manufact
uring_and_strength_evaluation_of_porous
_composites_based_on_numerical_simulat
ions/figures?lo=1

Real gas = ideal gas
very low pressure (P^{id})

$$\overline{S(P^{id})} = \overline{S'(P^{id})}$$

$$\overline{S(P^{id})} - \overline{S(1\ bar)}$$

$$= -\int_{1\ bar}^{P^{id}} \left(\frac{\partial \overline{V}}{\partial T}\right)_P dP$$

By using the equation of state for the real gas, we can evaluate this.

$$S°(1\ bar) - \overline{S'(P^{id})}$$

$$= -\int_{P^{id}}^{1\ bar} \frac{R}{P} dP$$

In this equation, the equation of state for a real gas is utilized.

(constant T)

$$\overline{S(1\ bar)}$$ Real gas
1 bar

Correction
for non-ideality

Hypothetical
ideal gas
1 bar
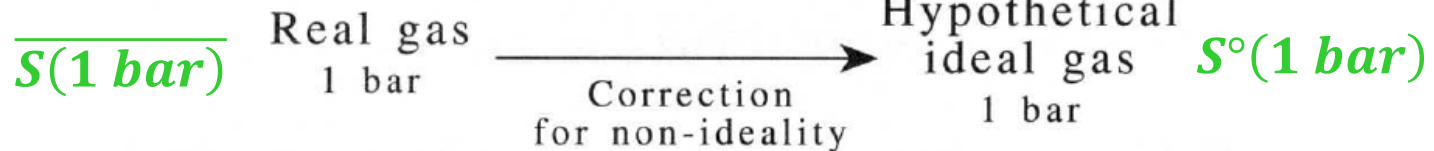
$$S°(1\ bar)$$

✓ P^{id} indicates that the pressure is low enough to assume the real gas perfectly behaves as an ideal gas.

✓ $S°(\mathbf{1\ bar})$ is the standard molar entropy of the gas. $\overline{S}$ is for the real gas and $\overline{S'}$ is for an ideal gas, and $S°$ is also for a (hypothetical) ideal gas.

✓ The non-ideality correction is give as:

$$[correction] = \overline{S(1\ bar)} - S°(1\ bar) = \int_{P^{id}}^{1\ bar} \left[\left(\frac{\partial \overline{V}}{\partial T}\right)_P - \frac{R}{P}\right] dP$$

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)

This is of ideal gas as

$$\Delta S = \int_{77.36}^{298.15} \frac{C_P(T')dT'}{T'}$$

$$= \int_{77.36}^{298.15} \frac{\frac{7}{2}RdT'}{T'} = \frac{7}{2}Rln[ln(T)]_{77.36}^{298.15}$$

$$= 39.25$$

TABLE 21.1

The standard molar entropy of nitrogen at 298.15 K.

Process	$\overline{S}^{\circ}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
0 to 10.00 K	2.05
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Total	191.6

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

✓ If a substance (material) does not change its phase (for example, not changing from liquid to gas, but keeping gas phase) during a process, we can calculate the difference in the enthalpy between two temperatures as:

$$H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_P(T)dT \quad \longleftarrow \quad \boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

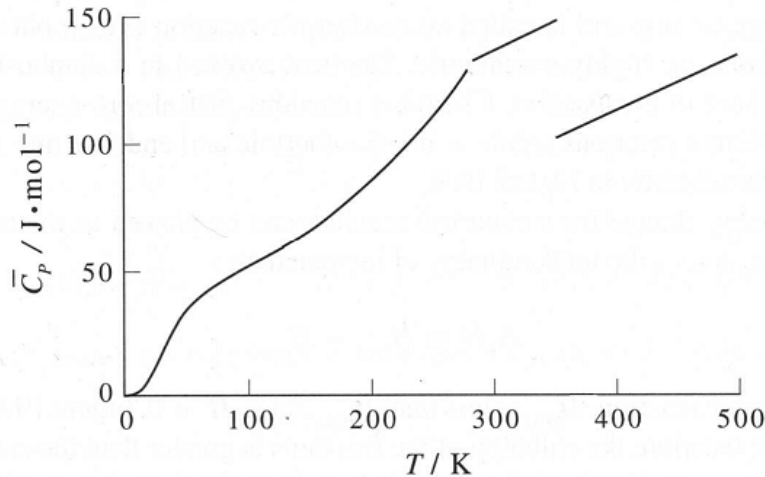*constant pressure between the two states (of different temperatures) are assumed.

✓ If there is a phase transition from solid to liquid (namely, melting) at T_{fus}, we need to consider it as:

$$H(T_2) - H(T_1) = \int_{T_1}^{T_{fus}} C_P{}^s(T)dT + \Delta_{fus}H + \int_{T_{fus}}^{T_2} C_P{}^l(T)dT$$

$$\Delta_{fus}H = H^l(T_{fus}) - H^s(T_{fus})$$

This $\Delta_{fus}H$ is called as "the heat of fusion".

- ✓ Example of C_p and H as a function of temperature: benzene (at 1 atm).
  - ✓ Melting point: 278.7 K
  - ✓ Boiling point: 353.2 K

- ✓ $\overline{C_P}$ means "constant-pressure molar heat capacity", which is "constant-pressure heat capacity per mole".
  - ✓ Remember "specific" is for "per kg" (per g).
- ✓ In the same manner, $\overline{H}$ is "molar enthalpy".

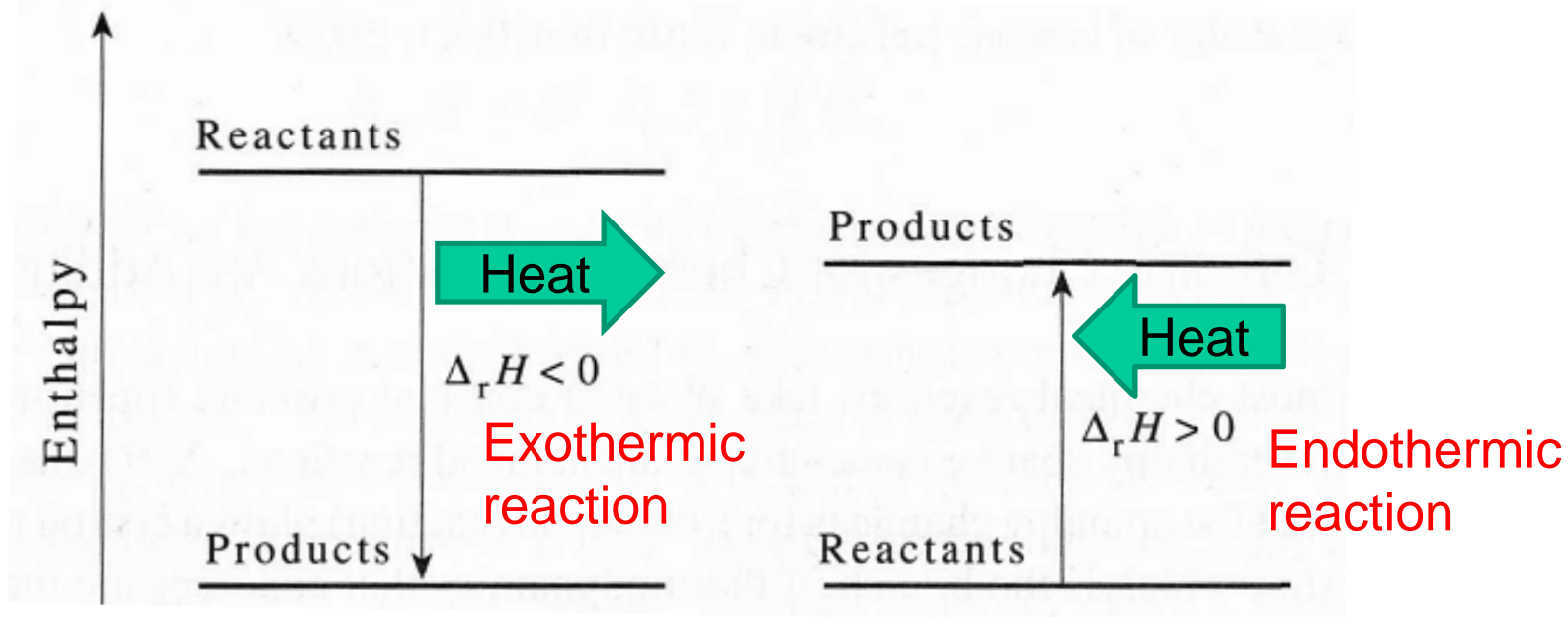- ✓ You can see a jump at a phase transition due to "latent heat".

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).
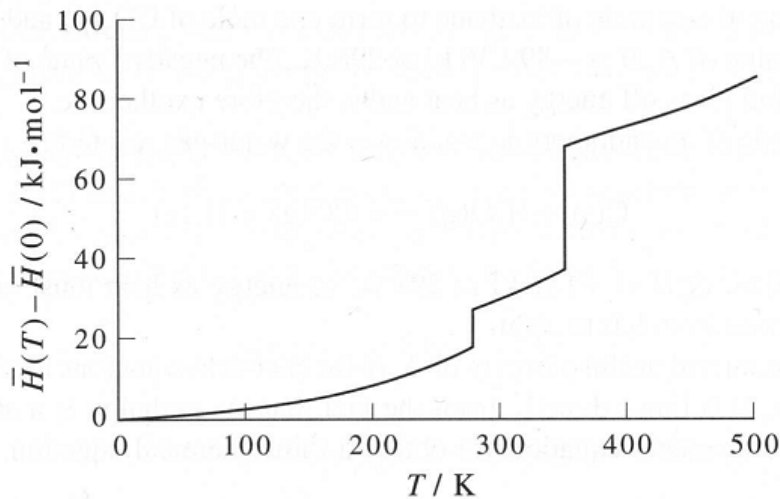
✓ Most chemical reactions take place at constant pressure (open to the atmosphere), the enthalpy change associated with chemical reactions is $\Delta_r H$ is important in thermochemistry.
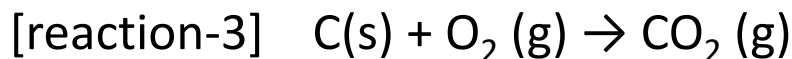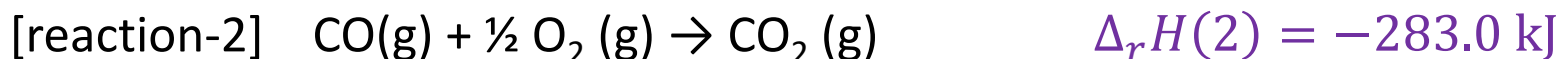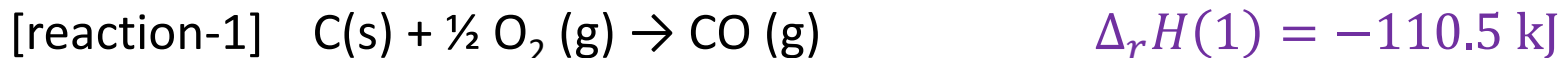
$$\Delta_r H = H_{products} - H_{reactants}$$

 ✓ If $\Delta_r H < 0$ ($q_P = \Delta_r H < 0$ and $H_{products} < H_{reactants}$), some energy as heat is released from the system. This reaction is exothermic.

 ✓ On the other hand, if $\Delta_r H > 0$ ($q_P = \Delta_r H > 0$ and $H_{products} > H_{reactants}$), and some energy as heat needs to be supplied to the system so as to drive the reaction. This reaction is endothermic.
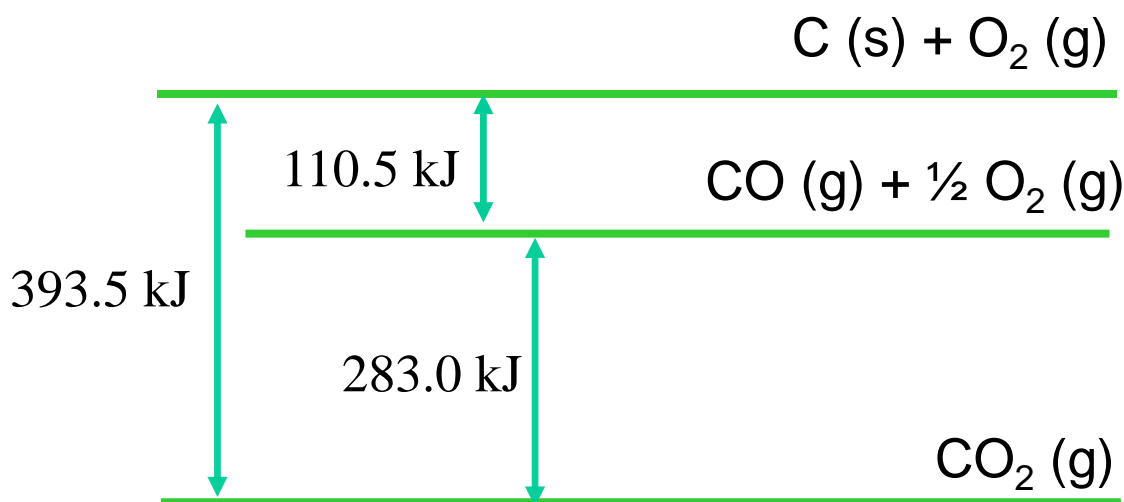
Reactants

Enthalpy

Heat

$\Delta_r H < 0$

Exothermic reaction

Products

Products

Heat

$\Delta_r H > 0$

Endothermic reaction

Reactants

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

✓ An important and useful property of $\Delta_r H$ for chemical equation is additivity, as enthalpy is a state function and is extensive quantity.

[reaction-1]   C(s) + ½ O$_2$ (g) → CO (g) $\Delta_r H(1) = -110.5$ kJ

[reaction-2]   CO(g) + ½ O$_2$ (g) → CO$_2$ (g) $\Delta_r H(2) = -283.0$ kJ

[reaction-3]   C(s) + O$_2$ (g) → CO$_2$ (g)

Due to the addtitivity $\Delta_r H(3) = \Delta_r H(1) + \Delta_r H(2)$
$$= -110.5 \text{ kJ} + (-283.0 \text{ kJ})$$
$$= -393.5 \text{ kJ}$$

C (s) + O$_2$ (g)
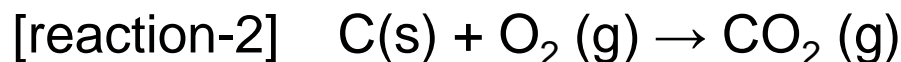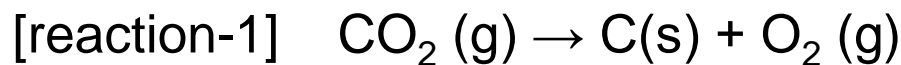
110.5 kJ

CO (g) + ½ O$_2$ (g)

393.5 kJ

283.0 kJ

CO$_2$ (g)

As enthalpy is a state function, we need to define "a state" for each system in order to calculate the enthalpy for each system.

✓ When a reaction is the reverse reaction of a certain reaction, e.g. reaction-2 is the reverse of reaction-1, as

[reaction-1] CO_2 (g) $\rightarrow$ C(s) + O_2 (g)

[reaction-2] C(s) + O_2 (g) $\rightarrow$ CO_2 (g)

we conclude from Hess's law that:

$$\Delta_r H(reverse) = -\Delta_r H(forward), \qquad \Delta_r H(1) = -\Delta_r H(2)$$

C (s) + O_2 (g)

393.5 kJ

+393.5 kJ

-393.5 kJ

CO_2 (g)

✓ The "standard reaction enthalpy", $\Delta_r H°$, and refers to the enthalpy change associated with one mole of a specified reagent (either a reactant or a product) when all reactants and products are in their "standard states".

✓ Recall that the "standard state":
  - ✓ 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.

✓ For example, we consider the combustion of carbon (thus the "specified reagent" is carbon here).

$$\text{[reaction]} \quad \text{C(s)} + \text{O}_2 \text{ (g)} \rightarrow \text{CO}_2 \text{ (g)} \qquad \Delta_r H° = -393.5 \text{ kJ mol}^{-1}$$
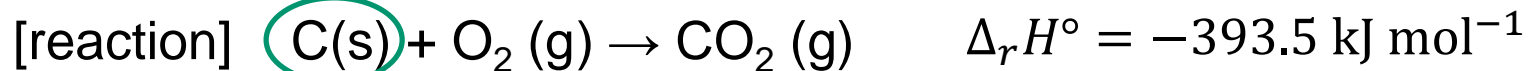
This "specified reagent" should be 1 mole.

✓ We can evaluate the reaction enthalpy for "2C(s) + 2O$_2$ (g) → 2CO$_2$ (g)" as
$$\Delta_r H = 2\Delta_r H° = -787.0 \text{ kJ mol}^{-1}.$$

✓ For specific reactions, we have special subscripts: like $\Delta_{vap}H°$, $\Delta_{c}H°$, etc.

TABLE 19.1

Common subscripts for the enthalpy changes of processes.

Subscript	Reaction
vap	Vaporization, evaporation
sub	Sublimation
fus	Melting, fusion
trs	Transition between phases in general
mix	Mixing
ads	Adsorption
c	Combustion
f	Formation

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

✓ The "standard molar enthalpy of formation", $\Delta_f H°$, is the standard reaction enthalpy for the formation of one mole of a molecule from its constituent elements. All reactants and products are in their standard states.

✓ For example, $\Delta_f H°$ of H_2O (l) is -285.8 kJ mol^{-1}, and the corresponding chemical equation is:

[reaction] $H_2(g) + ½ O_2(g) \rightarrow H_2O(l)$

This "specified reagent" should be 1 mole.
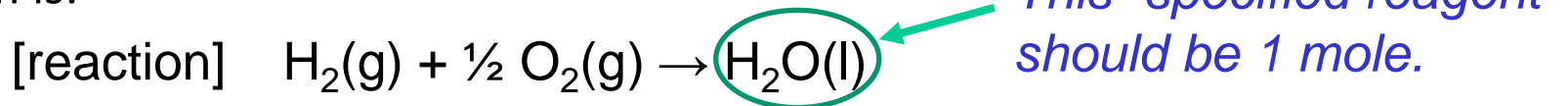
✓ The right figure is $\Delta_f H°$ for $CO_2(g)$, $H_2O(l)$ and $C_2H_2(g)$, based on the convention that $\Delta_f H° = 0$ for a pure element in its stable form at 1 bar and the temperature of interest.
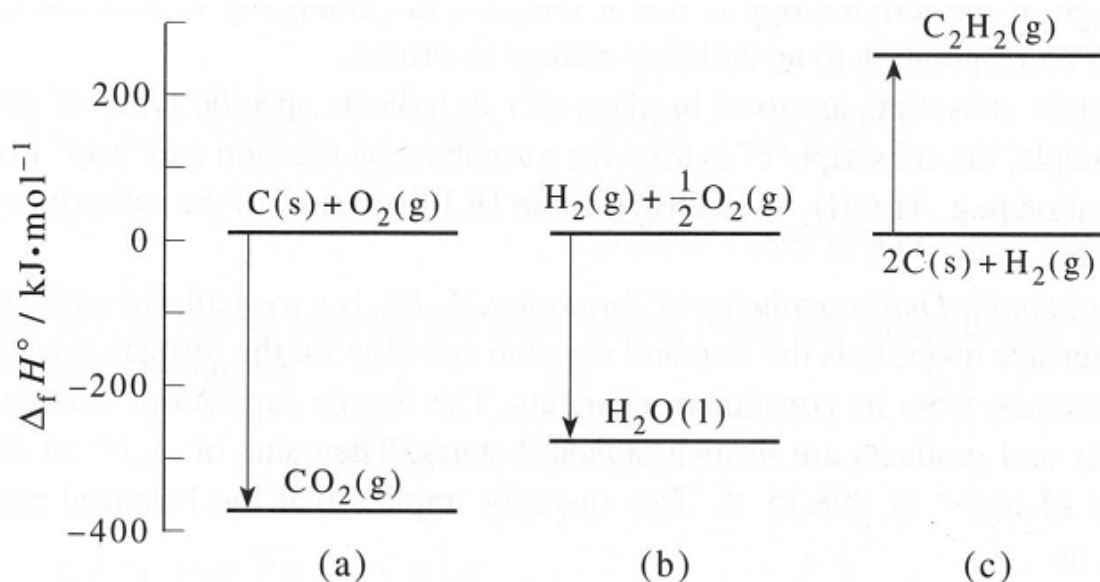
*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

✓ In a general reaction like "a A + b B → y Y + z Z", we do following steps.
  ✓ [step 1] decompose compounds A and B into their constituent elements,
  ✓ [step 2] combine the elements to form the compounds Y and Z.
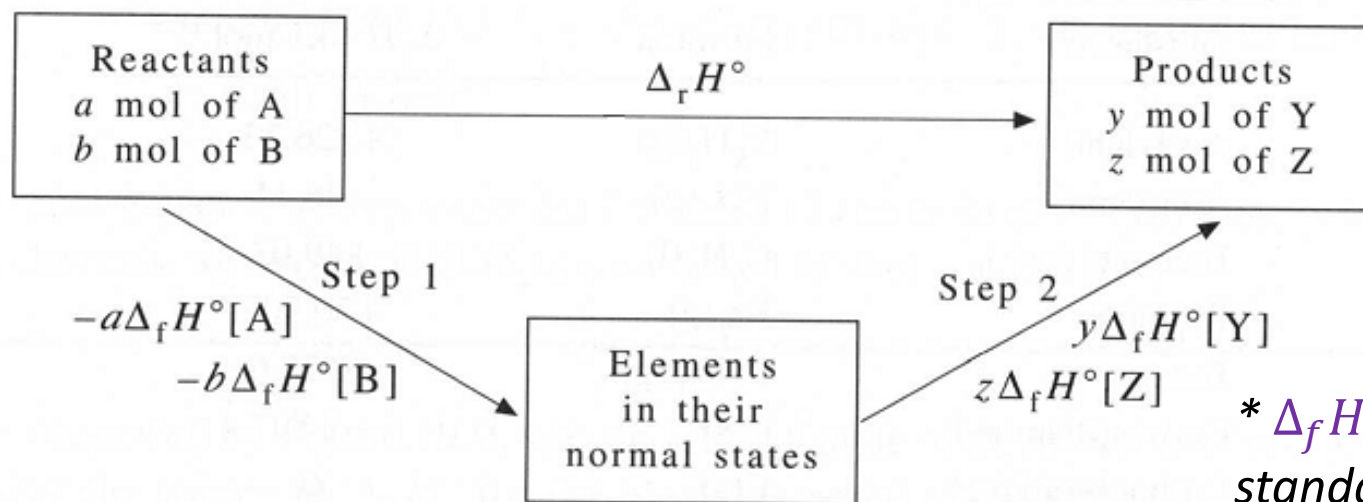
$* \Delta_f H°[A]$ denotes the standard molar enthalpy of formation for compound A.

$$\Delta_r H(1) = -a\,\Delta_f H°[A] - b\,\Delta_f H°[B],$$

$$\Delta_r H(2) = y\,\Delta_f H°[Y] + z\,\Delta_f H°[Z],$$

$$\Delta_r H = \Delta_r H(1) + \Delta_r H(2) = y\,\Delta_f H°[Y] + z\,\Delta_f H°[Z] - a\,\Delta_f H°[A] - b\,\Delta_f H°[B]$$

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

In a general reaction like "a A + b B → y Y + z Z", we do following steps.
- ✓ [step 1] decompose compounds A and B into their constituent elements,
- ✓ [step 2] combine the elements to form the compounds Y and Z.

$$\Delta_r H(1) = -a\,\Delta_f H°[A] - b\,\Delta_f H°[B], \qquad \Delta_r H(2) = y\,\Delta_f H°[Y] + z\,\Delta_f H°[Z]$$

$$\Delta_r H = \Delta_r H(1) + \Delta_r H(2) = \boldsymbol{y\,\Delta_f H°[Y] + z\,\Delta_f H°[Z] - a\,\Delta_f H°[A] - b\,\Delta_f H°[B]}$$

<example> $C_2H_2(g) + 5/2\ O_2(g) \rightarrow 2\ CO_2(g) + H_2O(l)$ at 298 K.

$$\Delta_r H$$
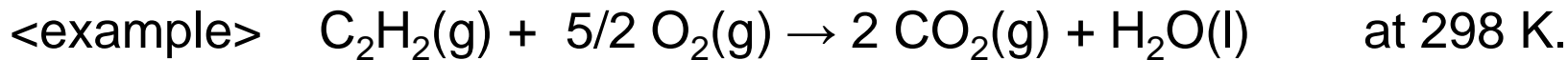
$$= (2)\,\Delta_f H°[CO_2(g)] + (1)\,\Delta_f H°[H_2O(l)] - (1)\Delta_f H°[C_2H_2(g)] - \left(\frac{5}{2}\right)\Delta_f H°[O_2(g)]$$

$$= 2 \times (-393.51\ \text{kJ mol}^{-1}) + (-285.83\ \text{kJ mol}^{-1}) - (+226.73\ \text{kJ mol}^{-1}) - \left(\frac{5}{2}\right)$$

$$\times (0\ \text{kJ mol}^{-1}) = -1299.58\ \text{kJ mol}^{-1}$$

As $O_2(g)$ is the stable state of oxygen at 298 K, $\Delta_f H°[O_2(g)]$ is 0 kJ mol^{-1}

✓ We consider a general reaction like "a A + b B → y Y + z Z" at other temperatures.

✓ It is calculable if we know the reaction enthalpy at a certain temperature and heat capacities of all reactants and products.

✓ Here assuming that we know the reaction enthalpy at temperature T$_1$, as $\Delta_r H(T_1)$. And we want to know that at temperature T$_2$.
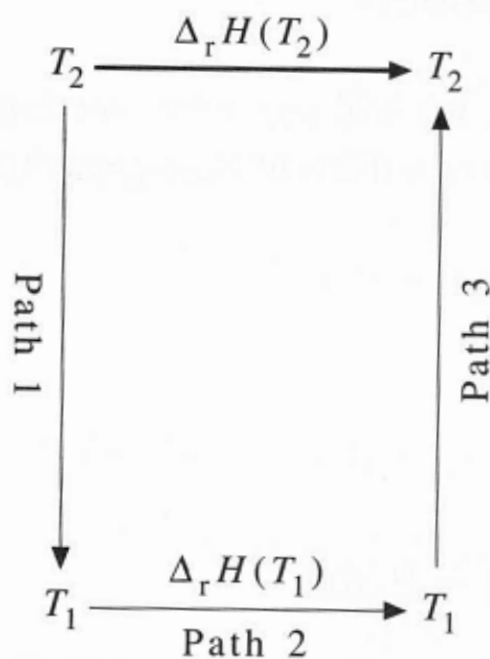
[Path 1] $\Delta H_1 = \int_{T_2}^{T_1} C_{P,reactants} dT = -\int_{T_1}^{T_2} C_{P,reactants} dT$

[Path 2] $\Delta H_2 = \Delta_r H(T_1)$

[Path 3] $\Delta H_3 = \int_{T_1}^{T_2} C_{P,products} dT$

$\Delta_r H(T_2) = \Delta H_1 + \Delta H_2 + \Delta H_3$

$= \Delta_r H(T_1) + \int_{T_1}^{T_2} (C_{P,products} - C_{P,reactants}) dT$

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

We consider a reversible process to show how to evaluate entropy change.

If we treat U and S as functions of V and T thus U(T, V) and S(T, V), their total derivatives are:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad and \quad dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

As the first and second laws for a reversible process:

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

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V$$

By substituting this equation to the first left one:

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV = \frac{C_V}{T} dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

In comparison with the total derivative of S given above:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad and \quad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

We consider a reversible process to show how to evaluate entropy change.

In the previous slide, we obtained:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

By making an integral with respect to T (with keeping V constant):

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_V(T)dT}{T} \qquad \text{(constant V)}$$

Hence, we can calculate S of an arbitrary temperature, S(T), if we know S(0 K):

$$S(T) = S(0\ K) + \int_0^T \frac{C_V(T')dT'}{T'} \qquad \text{(constant V)}$$

In an analogy, if we go through similar steps under constant pressure case (we start with the total derivative of H(S,P)):

$$S(T) = S(0\ K) + \int_0^T \frac{C_P(T')dT'}{T'} \qquad \text{(constant P)}$$

[Quiz] Show $S(T) = S(0\ K) + \int_0^T \dfrac{C_P(T')dT'}{T'}$

We consider a reversible process to show how to evaluate entropy change.

If we treat H and S as functions of T and P thus H(T, P) and S(T, P), their total derivatives are:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad and \quad dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

As the first and second laws for a reversible process:

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$
$$dH = d(U + PV) = TdS + VdP$$

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P$$

By substituting this equation to the first left one:

$$dS = \frac{1}{T}(dH - VdP) = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P dT + \frac{1}{T}\left[-V + \left(\frac{\partial H}{\partial P}\right)_T\right] dP = \frac{C_P}{T} dT + \frac{1}{T}\left[-V + \left(\frac{\partial H}{\partial P}\right)_T\right] dP$$

In comparison with the total derivative of S given above:

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad and \quad \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[-V + \left(\frac{\partial H}{\partial P}\right)_T\right]$$

We consider a reversible process to show how to evaluate entropy change.

In the previous slide, we obtained:

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

By making an integral with respect to T (with keeping P constant):

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Hence, we can calculate S of an arbitrary temperature, S(T), if we know S(0 K):

$$S(T) = S(0\ K) + \int_0^T \frac{C_P(T')dT'}{T'} \qquad \text{(constant P)}$$

✓ Nernst and Planck made a postulate corresponding to the third law:

Every substance has a finite positive entropy, but at zero kelvin the entropy may become zero, and does so in the case of a perfectly crystalline substance.
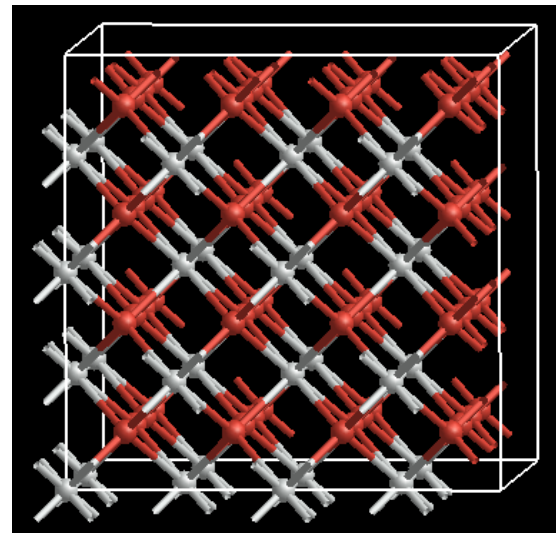
*We assume the state at 0 K is a perfect crystal. This is reasonable because
  ➢ A material becomes a solid at low temperatures.
  ➢ The lowest entropy (lowest disorder) must be achieved for the perfect crystal.

Liquid of UO_2
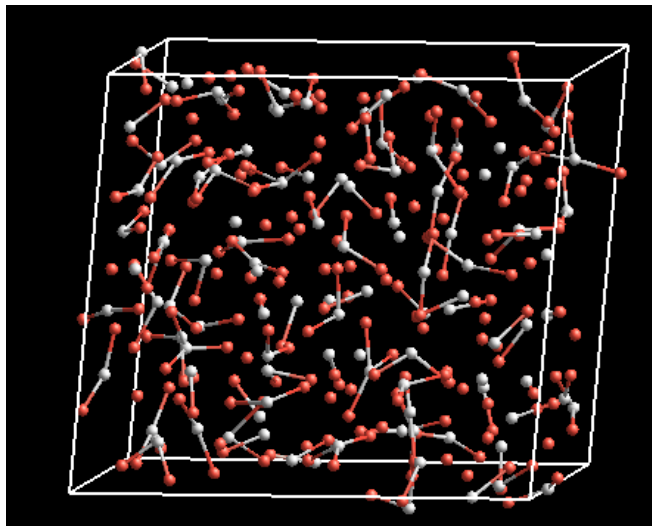
Perfect crystal of UO_2

We consider a case in which a phase transition is involved.

The entropy change upon the phase transition can be written as:

$$\Delta_{trs}S = \frac{q_{rev}}{T_{trs}}$$

Phase transition can be reversed by changing the temperature ever so slightly.

e.g.) melting of ice at 1 atm: the system will be all ice if T is slightly less than 273.15 K and all liquid if T is slightly greater than 273.15 K

Considering it takes place at a fixed temperature (T_{trs}) and under a constant pressure, $\Delta H = \Delta(U + PV) = \Delta U + P\Delta V = (q_P - P\Delta V) + P\Delta V = q_P$, then

$$\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$$

*$\Delta_{trs}H$ and $\Delta_{trs}S$ are the enthalpy and the entropy for the phase transition.

In a case in which melting is involved between 0 K and T K, for example:

$$S(T) = \int_0^{T_{fus}} \frac{C_P^s(T)dT}{T} + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_{fus}}^{T} \frac{C_P^l(T')dT'}{T'}$$

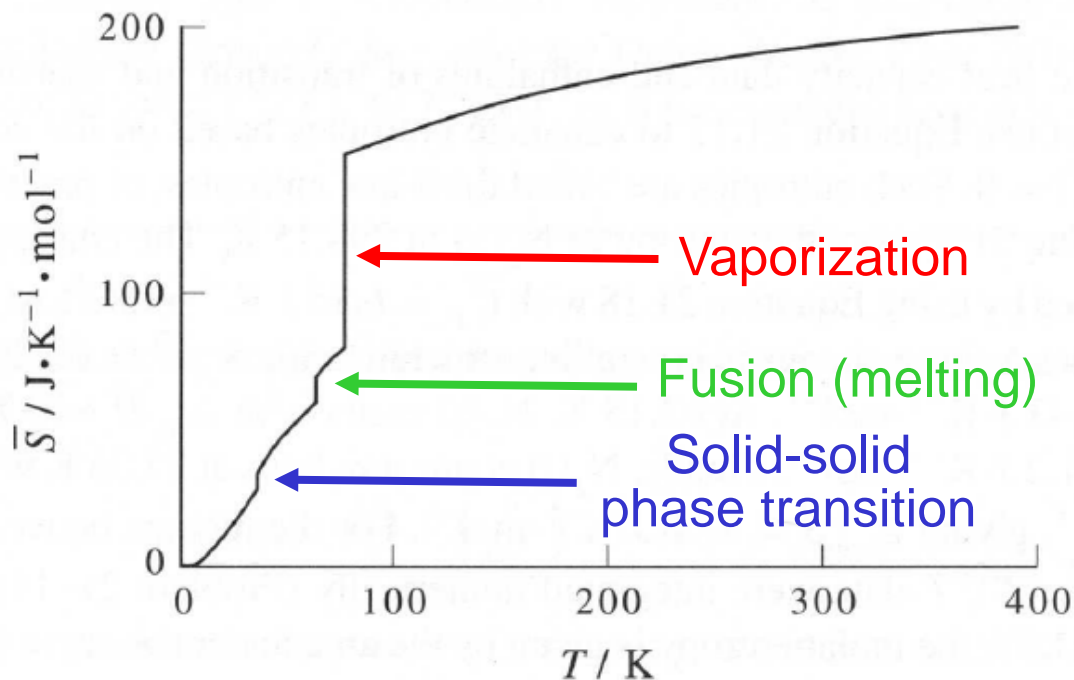*C_P^s and C_P^l are the heat capacity of the solid and the liquid, respectively.

✓ Because a hypothetical real gas is considered for "standard state of a gas", a correction due to non-ideality for the real gas is usually needed.

✓ Because the entropy is an index for disorder, the entropy for vaporization (l → g) is generally larger than the entropy for fusion (s → l), as expected.

TABLE 21.1
The standard molar entropy of nitrogen at 298.15 K.

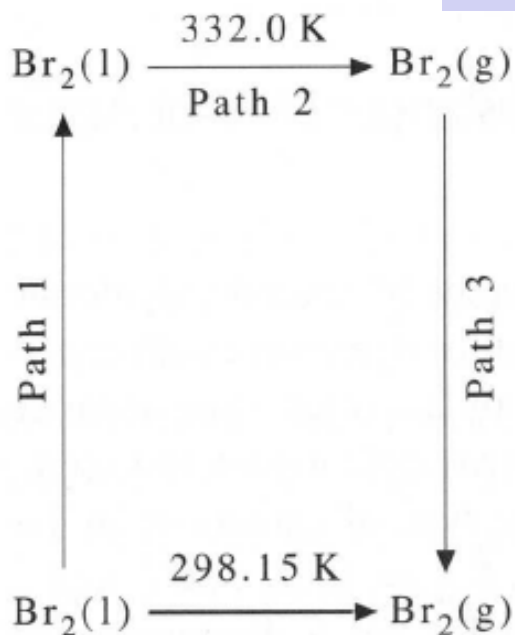| Process	$\overline{S}^{\circ}/J\cdot K^{-1}\cdot mol^{-1}$
0 to 10.00 K	2.05
10.00 to 35.61 K	25.79
Transition	6.43
35.61 to 63.15 K	23.41
Fusion	11.2
63.15 to 77.36 K	11.46
Vaporization	72.0
77.36 K to 298.15 K	39.25
Correction for nonideality	0.02
Total	191.6

Temperature dependence of the molar entropy of nitrogen

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

[Drill] Calcualte the standard molar entropy of $Br_2(g)$ @298.15 K.

$$Br_2(l) \xrightarrow[\text{Path 2}]{332.0\ K} Br_2(g)$$

Path 1

Path 3

$$Br_2(l) \xrightarrow{298.15\ K} Br_2(g)$$

- ✓ The normal boiling point of $Br_2(l)$: 332.0 K
- ✓ The standard molar entropy of $Br_2(l)$ @298.15 K:

$$\overline{S^{\circ}_{298}}[Br_2(l)] = 152.2\ \text{J K}^{-1}\ \text{mol}^{-1}$$

- ✓ The molar heat capacity of $Br_2(l)$:

$$\overline{C_P^l} = 75.69\ \text{J K}^{-1}\ \text{mol}^{-1}$$

- ✓ The molar heat capacity of $Br_2(g)$:

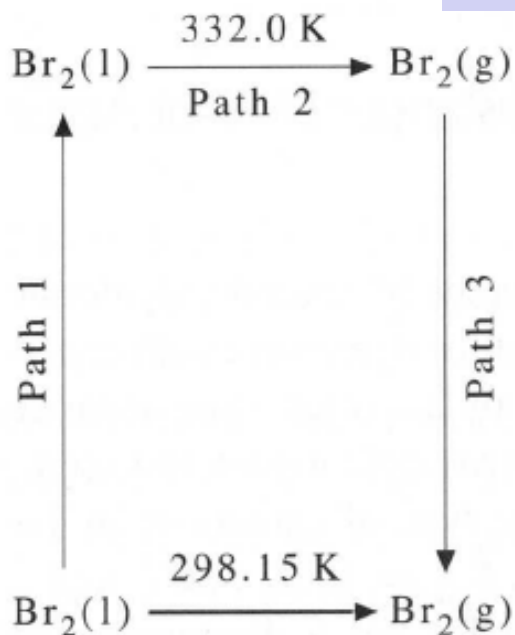$$\overline{C_P^g} = 36.02\ \text{J K}^{-1}\ \text{mol}^{-1}$$

- ✓ The molar enthalpy of vaporization at 332.0 K:

$$\Delta_{vap}\overline{H} = 29.54\ \text{kJ mol}^{-1}$$

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

[Drill] Calcualte the standard molar entropy of $Br_2(g)$ @298.15 K.

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✓ The standard molar entropy of $Br_2(l)$ @298.15 K:
$$\overline{S^{\circ}_{298}}[Br_2(l)] = 152.2 \text{ J K}^{-1} \text{ mol}^{-1}$$
✓ The molar heat capacity of $Br_2(l)$:
$$\overline{C_P^l} = 75.69 \text{ J K}^{-1} \text{ mol}^{-1}$$
✓ The molar heat capacity of $Br_2(g)$:
$$\overline{C_P^g} = 36.02 \text{ J K}^{-1} \text{ mol}^{-1}$$
✓ The molar enthalpy of vaporization at 332.0 K:
$$\Delta_{vap}\overline{H} = 29.54 \text{ kJ mol}^{-1}$$

<Path-1> $\Delta\overline{S_1} = \overline{S^l}(332.0\ K) - \overline{S^l}(298.15K) = \overline{C_P^l}\ln\frac{T_2}{T_1}$ = 8.140 J K^{-1} mol^{-1}

<Path-2> $\Delta\overline{S_2} = \overline{S^g}(332.0\ K) - \overline{S^l}(332.0K) = \frac{\Delta_{vap}\overline{H}}{T_{vap}}$ = 88.98 J K^{-1} mol^{-1}

<Path-3> $\Delta\overline{S_3} = \overline{S^g}(298.15\ K) - \overline{S^g}(332.0K) = \overline{C_P^g}\ln\frac{T_1}{T_2}$ =−3.970 J K^{-1} mol^{-1}

<In sum> $\overline{S^{\circ}_{298}}[Br_2(g)] = \overline{S^{\circ}_{298}}[Br_2(l)] + \Delta\overline{S_1} + \Delta\overline{S_2} + \Delta\overline{S_3}$= 245.5 J K^{-1} mol^{-1}

✓ As the same with enthalpy (i.e. standard molar enthalpy of formation), the standard molar entropies give us the entropy change by a chemical reaction.

✓ In a general case "a A + b B → y Y + z Z", for example, the standard entropy change is given by:

$$\Delta_r S^0 = y \times \bar{S}^\circ[Y] + z \times \bar{S}^\circ[Z] - a \times \bar{S}^\circ[A] - b \times \bar{S}^\circ[B]$$

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[Example] "H_2 (g) + ½ O_2 (g) → H_2O (l)", here $\bar{S}^\circ[H_2(g)]$=130.7 J K^{-1} mol^{-1}, $\bar{S}^\circ[O_2(g)]$=205.2 J K^{-1} mol^{-1}, $\bar{S}^\circ[H_2O(l)]$=70.0 J K^{-1} mol^{-1}.

$$\Delta_r S^0 = 1 \times 70.0 - 1 \times 130.7 - \frac{1}{2} \times 205.2 = -163.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

✓ If we use quantum-mechanics consideration on discretized energy levels and then statistical-thermodynamics consideration on how to occupy such discretized levels, we can evaluate the entropy in a theoretical manner.

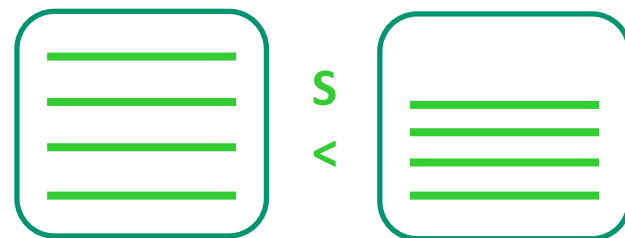| Gas	$\overline{S}°$(calc)/J·K^{-1}·mol^{-1}	$\overline{S}°$(exp)/J·K^{-1}·mol^{-1}
CO_2	213.8	213.7
NH_3	192.8	192.6
NO_2	240.1	240.2
CH_4	186.3	186.3
C_2H_2	200.9	200.8
C_2H_4	219.6	219.6
C_2H_6	229.6	229.5

Table: Comparison between calculated and experimental values on the standard molar entropies of several polyatomic gasses at 298.15 K and 1 bar.

✓ [$21.8] Sometimes, we can see a large difference between experiment and calculation. (e.g. for CO, $\overline{S_{calc}}$=160.3 J K^{-1} mol^{-1}; $\overline{S_{exp}}$=155.6 J K^{-1} mol^{-1}) The difference $\overline{S_{calc}} - \overline{S_{exp}}$ (>0, usually) is called as "residual entropy", and can be explained by considering weak interaction between molecules.

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

There are some trends in standard molar entropies. (the table for 298.15 K)

Substance	$\overline{S}°/J \cdot K^{-1} \cdot mol^{-1}$	Substance	$\overline{S}°/J \cdot K^{-1} \cdot mol^{-1}$
$Ag(s)$	42.55	$HCl(g)$	186.9
$Ar(g)$	154.8	$HCN(g)$	201.8
$Br_2(g)$	245.5	$HI(g)$	206.6
$Br_2(l)$	152.2	$H_2O(g)$	188.8
$C(s)(diamond)$	2.38	$H_2O(l)$	70.0
$C(s)(graphite)$	5.74	$Hg(l)$	75.9
$CH_4(g)$	186.3	$I_2(s)$	116.1
$C_2H_2(g)$	200.9	$I_2(g)$	260.7
$C_2H_4(g)$	219.6	$K(s)$	64.7
$C_2H_6(g)$	229.6	$N_2(g)$	191.6
$CH_3OH(l)$	126.8	$Na(s)$	51.3
$CH_3Cl(g)$	234.6	$NH_3(g)$	192.8
$CO(g)$	197.7	$NO(g)$	210.8
$CO_2(g)$	213.8	$NO_2(g)$	240.1
$Cl_2(g)$	223.1	$O_2(g)$	205.2
$H_2(g)$	130.7	$O_3(g)$	238.9
$HBr(g)$	198.7	$SO_2(g)$	248.2

➢ The standard molar entropies of gasses are larger than those of solids. Those for liquids are in between.

>> Because the entropy indicates the degree of disorder.

➢ The more atoms of a given type in a molecule, the greater is its entropy. (C_2H_2, C_2H_4, and C_2H_6)
>> As the greater is the capacity of the molecule to take up energy, because more "vibrational and rotational energy levels" are available.

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

✓ There are some trends in standard molar entropies. (the table for 298.15 K)

   ➢ An increase in mass leads to an increase in entropy.

>> As thermal disorder increases, because "more translational energy levels are available" (according to quantum mechanics, and then statistical thermodynamics)
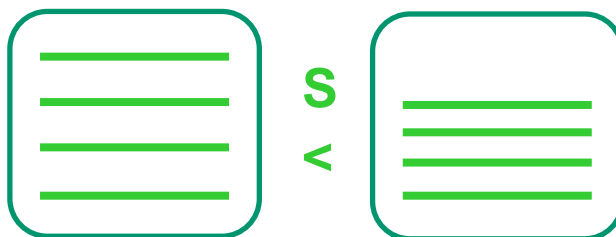
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TABLE 21.3

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

Noble gas	$\overline{S}^{\circ}/J \cdot K^{-1} \cdot mol^{-1}$	Halogen	$\overline{S}^{\circ}/J \cdot K^{-1} \cdot mol^{-1}$	Hydrogen halide	$\overline{S}^{\circ}/J \cdot K^{-1} \cdot mol^{-1}$
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).
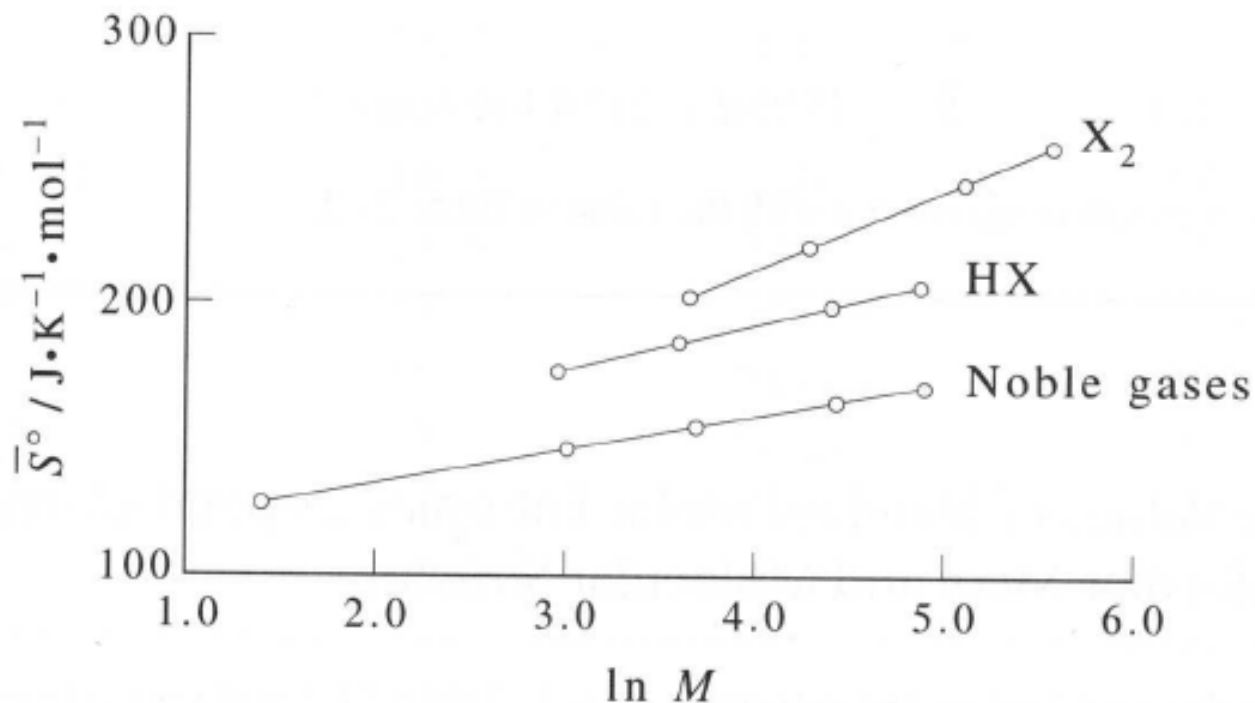
FIGURE 21.3
Standard molar entropies ($\overline{S}^{\circ}$) for the noble gases, the gaseous halogens, and the hydrogen halides at 298.15 K plotted against ln M, where M is the molecular mass.

If we consider the degree of disorder, in quantum mechanics and statistical thermodynamics, entropy is understandable and indeed can be calculated.
(may be learned in a future lecture)

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