Physical Chemistry for Energy Engineering (Homework-02 answers)

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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).

HW02-01 [5pt in total]

<evaluation elements>

- ✓ If you make any mistake, no point.

[HW02-01] Derive Maxwell relations for Helmholtz energy.

Differential equation of Helmholtz energy ($A = U - TS$) is:

$$dA = dU - TdS - SdT$$

Considering a process along a reversible path (and thus for processes of thermodynamical equilibrium states), the first law is:

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

Hence,

$$dA = -PdV - SdT$$

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

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

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

Since, the cross derivatives are equal as: $\left(\frac{\partial^2 A}{\partial T \partial V}\right) = \left(\frac{\partial^2 A}{\partial V \partial T}\right)$

Then, Maxwell relation for Helmholtz energy is $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

HW02-02 [8pt in total]

[HW02-02] Calculate $(\partial U/\partial V)_T$ for (1) a gas that obeys the equation of state for ideal gas and (2) a gas obeys the van der Waals equation. Then, discuss the difference between gas (1) and gas (2) in 150 words or less. Note that van der Waals equation gives more accurate description of a real gas: parameter a reflects the inter-molecular (attractive) interaction and parameter b reflects the molecular size. The van der Waals equation is:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

*Hint: you cannot directly calculate $(\partial U/\partial V)_T$. Instead, you should use some relation in the derivation of Maxwell relations for internal energy and Helmholtz energy.

*There was a mistake: van der Waals equation should be with molar volume, not volume.

Considering a process along a reversible path (and thus for thermodynamical equilibrium states), the first law is:

$$dU = TdS - PdV$$

Taking partial derivative of the 1st law eq. regarding V with fixing T gives:

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

Then, using the Maxwell relation for Helmholtz energy, $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$:

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

2pt for the equation derivation

This equation is to be used to evaluate $\left(\frac{\partial U}{\partial V}\right)_T$ for vdW gas.

HW02-02 [8pt in total]

[HW02-02] Calculate $(\partial U/\partial V)_T$ for (1) a gas that obeys the equation of state for ideal gas and (2) a gas obeys the van der Waals equation. Then, discuss the difference between gas (1) and gas (2) in 150 words or less. Note that van der Waals equation gives more accurate description of a real gas: parameter a reflects the inter-molecular (attractive) interaction and parameter b reflects the molecular size. The van der Waals equation is: $P = \frac{RT}{V-b} - \frac{a}{V^2}$

(1) <Ideal gas>

For ideal gas, as the internal energy only depends on temperature, $\left(\frac{\partial U}{\partial V}\right)_T = 0$, or

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left(\frac{\partial\left(\frac{nRT}{V}\right)}{\partial T}\right)_V - \frac{nRT}{V} = 0$$

2pt for ideal gas

(2) <vdW gas>

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left(\frac{R}{V-b}\right) - \left(\frac{RT}{V-b} - \frac{a}{V^2}\right) = \frac{a}{V^2} > 0$$

2pt for vdW gas

<Explanation on the difference>

- ✓ vdW-gas result means that the internal energy increases as the volume increases This is due to inter-molecular binding interaction, as a is involved in the equation.
- ✓ Because inter-molecular interactions are neglected in ideal gas, it is reasonable that $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for ideal gas.

2pt for these points

HW02-03 [6pt in total]

<evaluation elements>

✓ If you write equations using "Δ" (like ΔU) not "d" (like $\mathrm{d}U$), -3pt.

[HW02-03] Starting from the 2nd of thermodynamics, namely

> *"There is a thermodynamic state function of a system called as entropy, S, such that for any change in the thermodynamic state of the system, $dS \geq \frac{\delta q}{T}$, where the equality sign applies if the change is carried out reversibly and the inequality sign applies if the change is carried out irreversibly at any stage.",*

please derive a condition to judge using Gibbs energy whether a given chemical reaction can simultaneously take place or not at constant-T constant-P conditions.

As the first law: $dU = \delta q + \delta w$, *and* $\delta w = -P_{external} dV$

As a const.-P system, if the process is quasi-static, it is OK to assume that $P_{ext}=P_{sys}$. Thus, $\delta w = -PdV$ *. Hence,* $dU + PdV = d(U+PV) = \delta q$

$$dH = \delta q$$

Here, we apply the equation above into the second law ($dS \geq \delta q/T$)

$$dH \leq TdS \quad \text{(for const.-P)}$$

for const.-P condition, where the equal sign is for reversible process and the unequal sign for irreversible process.

2pt for this equation of 2nd law for const.-P condition

HW02-03 [6pt in total]

[HW02-03] Starting from the 2nd of thermodynamics, namely

> "*There is a thermodynamic state function of a system called as entropy, S, such that for any change in the thermodynamic state of the system,* $dS \geq \frac{\delta q}{T}$*, where the equality sign applies if the change is carried out reversibly and the inequality sign applies if the change is carried out irreversibly at any stage.*",

please derive a condition to judge using Gibbs energy whether a given chemical reaction can simultaneously take place or not at constant-T constant-P conditions.

In constant-T condition, the differential of Gibbs energy is written as:

$$dG = dH - TdS - SdT = dH - TdS \quad \textit{[quasi-static const.-T]}$$

If we introduce this relation into the equation to judge whether the process is reversible or irreversible:

$$dH - TdS = dG \leq 0 \quad \textit{[quasi-static const.-T const.-P]}$$

$$dG = d(H - TS) = 0 \quad \textit{[rev. const-T const.-P]}$$

2pt for this dG=0 equation for reversible const.-T const.-P condition.

In summary, dG is a good index to judge the reaction direction:$dG \leq 0$ where the equal sign is for equilibrium state (reversible process) and the unequal sign for spontaneous process (irreversible process).

2pt for combining 2 equations to prove dG is a good index.

HW02-04 [6pt in total; 2pt for each]

[HW02-04] Please judge whether the following statement is correct or not. If not, please modify it.
(1) The initial state of spontaneous reaction must be a thermodynamical equilibrium state.
>> Wrong: if the initial state is a thermodynamical equilibrium state, at which any thermodynamical quantity is temporally and spatially uniform, no reaction can spontaneously take place. By replacing "equilibrium" with "non-equilibrium", the sentence becomes correct.

(2) The condition for thermodynamical equilibrium state and reversible process is identical, because thermodynamical equilibrium states are assumed in reversible processes.
>>This statement was confusing and inappropriate. Why the condition of thermodynamical equilibrium state is the same with reversible process is explained in the material of #10 (see the next slide).

(3) For a closed system, if there is a reaction which holds "$dS > 0$", the reaction should proceed spontaneously.
>> Wrong: "$dS > 0$" is the condition of spontaneous process for isolated systems. By replacing "closed system" with "isolated system" the sentence becomes correct.

(#10 lecture) 2.1.1. Direction of spontaneous system evolution

- $20.4: The second law of thermodynamics states that the entropy of an isolated system increases as a result of a spontaneous process -

- ✓ To focus on the entropy only (excluding an energy-driven spontaneous process), we consider an isolated system where the energy is conserved. As the system is isolated and thus no heat transfer occurs, if the entropy increases, it should be the one generated within the system itself.

  *Note that entropy is not necessarily conserved, unlike energy.
- ✓ In isolated systems, irreversible process causes an increase in the entropy ($dS>0$), according to the second low.
- ✓ For an irreversible process, some unbalance in temperature, pressure, etc (or some non-uniformity in the system) initially exist between the system and the surroundings or inside the system (e.g. multiple sub-systems including regions of different temperatures, which we took as an example in #10 lecture).
  - ✓ In the case of isolated system, because there is not energy/matter exchange with surroundings, such unbalance should be inside the system (again, we consider such case in #10 lecture as an example)
  - ✓ Due to such an unbalance, the system suffers some change to mitigate/expel the unbalance. For example, heat transfer, expansion/compression, mixing, etc, which we know spontaneously occur. Thus, irreversible processes that can occur with conserving the condition of “isolated” are basically spontaneous processes.

(#10 lcture) 2.1.3. Summary of processes - spontaneous reaction -

- ✓ For a reversible process, we need to introduce an infinitesimal change in the system.
  - ✓ For example, in a “thermally isolated system” where an energy transfer by heat is not allowed but by work is allowed (thus, the process is adiabatic), to cause an reversible adiabatic expansion, we need to infinitesimally decrease the external pressure with keeping $P_{ext}=P$ (this is conceptual; not possible in reality).
  - ✓ So, if we do not introduce an infinitesimal change, nothing occurs in such a system. The system eternally stays at a stationary state, which an (thermodynamical) equilibrium state.
  - ✓ In other words, a system that can go thorough a reversible process is basically at an equilibrium state.

- ✓ As definition, a spontaneous process proceeds without any manipulations of the system and/or the surroundings.
  - ✓ Thus, as definition, the initial state of the system should be an non-equilibrium state because no (macroscopic) change occurs in the equilibrium state. And thus, a spontaneous process must be an irreversible process.

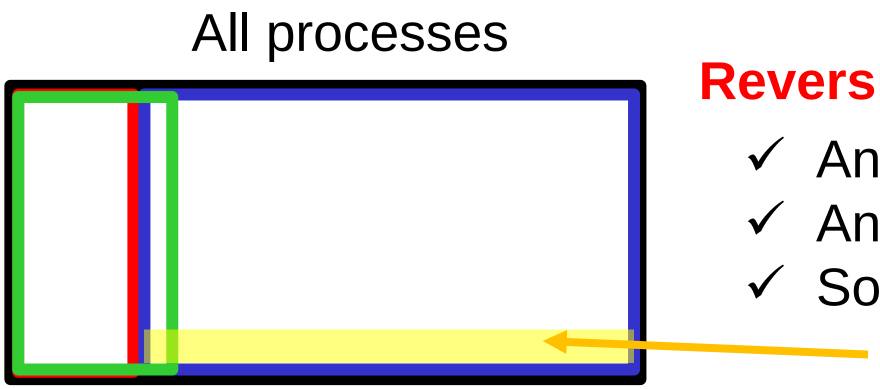
- ✓ Any process is rev. or irrev.
- ✓ Any rev. process is quasi-static.
- ✓ Some irrev. process is quasi-static.

- ✓ <Quasi-static process> process from a state to another state. During the process, the system or all sub-systems in the system are always at some states where we can define state functions. (I wrote in the lecture material “at some equilibrium states”, but it was wrong.)
- ✓ <Reversible process> process from one equilibrium state to another equilibrium state. During the process, the system is always at some equilibrium state. Because we can always define state functions at equilibrium states, and the system is always at an equilibrium state during a reversible process, the reversible process is always quasi-static from the definition.
    - ➢ For an isolated system, $dS = 0$ is the condition. Because the reversible process assumes the system is currently at an equilibrium state, if there is a reversible process for the system at present (and thus $dS = 0$) we can also say the system is at an equilibrium state.
- ➢ <Equilibrium state> If there is a reversible process ($dS = 0$) for the system of interest, we can say the system is at equilibrium. But, we just confirmed here this is sufficient, but not confirmed this is necessary. We will check it later.

- ✓ <Irreversible process> processes other than reversible processes. We may / may not define thermodynamic quantities during the process.
  - ➢ For an isolated system , if quasi-static (we can define dS), $dS > 0$
- ✓ <Spontaneous process> process from a non-equilibrium state to an equilibrium or to a non-equilibrium state. The initial state of spontaneous process must be a non-equilibrium state. We may / may not define thermodynamic quantities during the process. This cannot be a reversible process because reversible process does not spontaneously occur.
  - ➢ For an isolated system, if quasi-static (we can define dS), $dS > 0$. This condition is sufficient and necessary for a spontaneous process.
- ➢ <Non-equilibrium state> If there is a spontaneous process ($dS > 0$) in the system of interest, the system is at an non-equilibrium state. Thus, $dS > 0$ is sufficient and necessary for non-equilibrium state.

- ➢ <Some unrealistic processes> We can imaginary consider some unrealistic processes, such as “there are two sub-systems having temperatures 300 K and 400 K in an isolated system, and the temperature will change to 200 K and 500 K”., which satisfies the first law but not the second law In this case, $dS < 0$ (and $dS < 0$) can be achieved. Unless “isolated” condition is lifted, such a process never occurs in reality according to the second law.

In lecture #10, I shows the following figure.

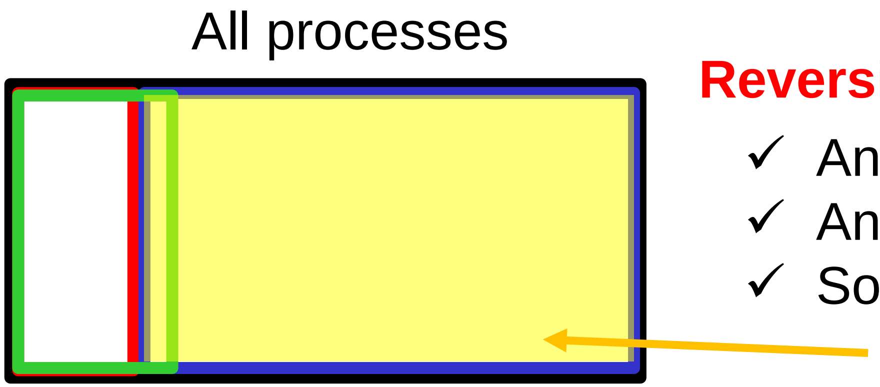


Reversible **Irreversible** **Quasi-static**

- ✓ Any process is rev. or irrev.
- ✓ Any rev. process is quasi-static.
- ✓ Some irrev. process is quasi-static.

spontaneous

But, the following figure would be more appropriate because there is no irreversible process that satisfies the condition such as “isolated”, “const.-T const.-P” but are not spontaneous, as far as I consider. (Please also consider by yourself whether realistic irreversible processes that are not spontaneous exist or not.)

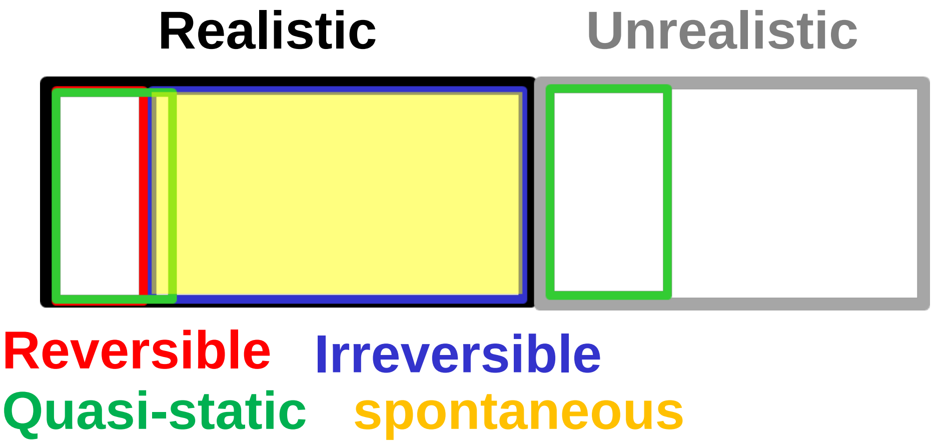


Reversible **Irreversible** **Quasi-static**

- ✓ Any process is rev. or irrev.
- ✓ Any rev. process is quasi-static.
- ✓ Some irrev. process is quasi-static.

spontaneous

And, adding some “unrealistic processes” that violates the second law but not the first law), which never happen in reality, we can express processes by the following figure



*Strictly speaking, “reversible” and “quasi-static” are also not realistic, it can be considered as a idealistic limit of realistic processes. Thus, we can consider they are conceptually realistic. On the other hand, “unrealistic processes” here are totally unrealistic. Even in some ideal conditions, they never occur.

In this figure, we have 5 regions and each has the condition on dS:

(1) Reversible (which is always quais-static): $dS = 0$

(2) Irreversible/spontaneous and quasi-static: $dS > 0$

(3) Irrevesible/spontaneous and non-quasi-static: $\Delta S > 0$ if state functions can be defined at the initial and final points of the process.

(4) “Unrealistic” and quasi-static: $dS < 0$

(5) “Unrealistic” and non-quasi-static: $\Delta S < 0$ if state functions can be defined at the initial and final points of the process.

And (1) is a sufficient condition for equilibrium state and (2) is a sufficient and necessary conditions for non-equilibrium state.

#10, 11: Extension to “const.-T const.-V” or “const.-T const.-P” conditions

- ✓ Stating with the discussion on the isolated system, we extend the theory to “const.-T const.-V” or “const.-T const.-P” systems.
  - ✓ [const.-T const.-V] $dA = 0$ is sufficient for equilibrium state; $dA < 0$ is sufficient and necessary for non-equilibrium state;
  - ✓ [const.-T const.-P] $dG = 0$ is sufficient for equilibrium state; $dG < 0$ is sufficient and necessary for non-equilibrium state;

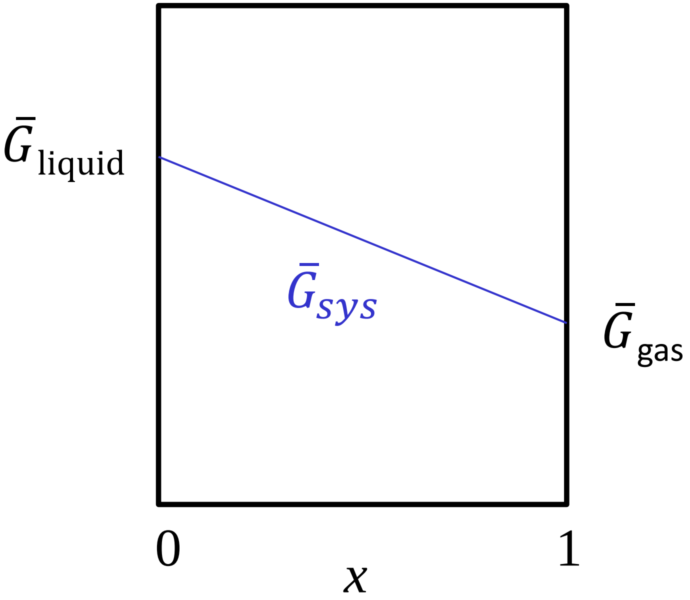
- ✓ We discuss why “dG=0 is just sufficient but not necessary for equilibrium state. This discussion can be applied for “dS=0 is not necessary” and “dA=0 is not necessary” for isolated and “const.-T const.-V” conditions.
- ✓ One typical case is “water at 500 K, 1 bar” (next page). In this case, we know that the equilibrium phase is gas, and no coexistence of liquid and solid waters. For example, if we draw a x-G graph, where x is a molar fraction of gas phase and (1-x) is a molar fraction of liquid phase. As the molar Gibbs energy of gas ($\bar{G}_{\text{gas}}$) is lower than the molar Gibbs energy of liquid ($\bar{G}_{\text{liquid}}$)

In this case, we know that the equilibrium phase is gas, and no coexistence of liquid and solid waters. For example, if we draw a x-G graph, where x is a molar fraction of gas phase and (1-x) is a molar fraction of liquid phase. The molar Gibbs energies of gas and liquid waters are defined as $\bar{G}_{\mathrm{gas}}$ and $\bar{G}_{\mathrm{liquid}}$, respectively, which are constant. Then, the system molar Gibbs energy ($\bar{G}_{\mathrm{sys}}$) is given as

$$\bar{G}_{sys} = x\bar{G}_{gas} + (1 - x)\bar{G}_{liquid}$$

which is a function of *x*.

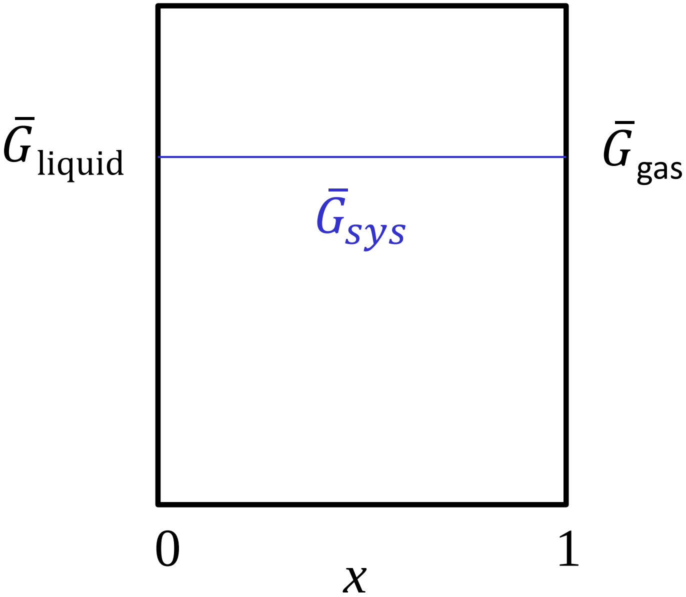
As $\bar{G}_{\mathrm{gas}} < \bar{G}_{\mathrm{liquid}}$ in "water at 500 K, 1 bar" condition, the system Gibbs energy is given as in the figure below.



In this case, if x<1, the system is non-equilibrium because we can find a process that gives $\frac{d\bar{G}_{sys}}{dx} < 0$, which is a spontaneous process. However, at x=1, $\frac{d\bar{G}_{sys}}{dx} = 0$ is not satisfied although it is an equilibrium state.

Indeed, at x=1, there is no "realistic process": Specifically, there is no reversible process and no irreversible process. Only there is an unrealistic process that causes $d\bar{G}_{sys} > 0$. Thus, "there is no possible realistic process" can be also a sufficient condition for equilibrium state.

Indeed, for a single-component phase equilibrium, “there is no possible realistic process” usually occurs as a condition for equilibrium state. Only the case such as “373 K, 1 bar , water”, which is the coexisting condition of liquid and gas phases, “dG=0” is achieved as a condition of equilibrium state. In “373 K, 1 bar , water”, $\bar{G}_{\text{gas}} = \bar{G}_{\text{liquid}}$ is achieved and $d\bar{G}_{sys} = 0$ is satisfied in all x. This means “liquid water”, “liquid and gas water mixture”, “gas water” are at equilibrium states of “373 K, 1 bar , water” system. If we start with “liquid water”, by infinitesimally adding heat with satisfying “const.-T and const.-P”, the system gradually moves to ““liquid and gas water mixture” and then to ““gas water”. Such process induced by a infinitesimal change is reversible process. At any moment, if you stop the infinitesimal addition of heat, the process stops.



*However, in the case of chemical equilibrium, “dG=0” is more often found as a condition of equilibirium state, we have been studying it recently.

HW02-05 [3pt (0pt if any mistake)]

[HW02-05] Derive the Gibbs –Helmholtz equation: $\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2}$

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

Considering partial derivative with respect to T keeping P fixed gives:

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

Then, for reversible processes (*dU=TdS-PdV*), $dH = dU + d(PV) = TdS - PdV + PdV + VdP = TdS + VdP$.

Considering partial derivative with respect to T keeping P fixed gives

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

Applying this relation above, then we obtain:

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

HW02-06 [10pt in total: (1) 2pt, (2) 4pt, (3) 4pt]

<evaluation elements for (1)>

- ✓ If you forget the unit, 0 pt. If any mistake, 0 pt.

[HW02-06:#19-36] (1) Given the following data at 298.15 K and 1 bar:

$$\frac{1}{2}\mathrm{H_2(g)} + \frac{1}{2}\mathrm{F_2(g)} \rightarrow \mathrm{HF(g)}, \qquad \Delta_{r1}\mathrm{H}^\circ = -273\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{H_2(g)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{H_2O(l)}, \qquad \Delta_{r2}\mathrm{H}^\circ = -286\ \mathrm{kJ\ mol^{-1}}$$

Use these data to calculate the value of $\Delta_r\mathrm{H}$ at 298.15 K and 1 bar for the reaction described by

$$\mathrm{2F_2(g) + 2H_2O(l) \rightarrow 4HF(g) + O_2(g)}$$

<Solution-1>To construct the target chemical equation by using the 2 given chemical equations, we should do “$4 \times (eq.1) - 2 \times (eq.2)$”.
Then, $\Delta_r\mathrm{H}^\circ = 4 \times \Delta_{r1}\mathrm{H}^\circ - 2 \times \Delta_{r2}\mathrm{H}^\circ = -520\ \mathrm{kJ\ mol^{-1}}$.

<Solution-2> The given equations are for formation reactions of HF(g) and H_2O(l). Therefore, $\Delta_{r1}\mathrm{H}^\circ = \Delta_f\mathrm{H}^\circ(\mathrm{HF(g)})$ and $\Delta_{r2}\mathrm{H}^\circ = \Delta_f\mathrm{H}^\circ(\mathrm{H_2O(l)})$. Then,

$$\Delta_r\mathrm{H} = \sum_{\text{products}} \Delta_f\mathrm{H}^\circ - \sum_{\text{reactants}} \Delta_f\mathrm{H}^\circ$$

$$= \left\{4\Delta_f\mathrm{H}^\circ\left(\mathrm{HF(g)}\right) + \Delta_f\mathrm{H}^\circ\left(\mathrm{O_2(g)}\right)\right\} - \left\{2\Delta_f\mathrm{H}^\circ\left(\mathrm{F_2(g)}\right) + 2\Delta_f\mathrm{H}^\circ\left(\mathrm{H_2O(l)}\right)\right\} = \cdots$$

HW02-06 [10pt in total: (1) 2pt, (2) 4pt, (3) 4pt]

[HW02-06:#19-36] (2) Please determine whether this reaction proceeds spontaneously or not at const.-T and const.-P condition (298.15 K and 1 bar). You need to clearly explain the reason of the judgment in 150 words or less. (*Hint: you need not to exactly know Gibbs energy for this problem. Instead, you can use the tendency of entropy of gas, liquid and solid phases together with the result of (1).)

Gibbs energy is defined as: $G = H - TS$

The differential equation is: $dG = dH - TdS - SdT = dH - TdS$

where we use $dT = 0$ as const.-T condition.

Now, we are comparing Gibbs energies of 2 systems. Thus, integral form is more easy to use as: $\Delta G = \int dG = \int dH - \int TdS = \int dH - T\int dS = \Delta H - T\Delta S$

where T was taken out of the integral as const.-T condition.

Then, in (1), ΔH was determined as $-520\ \mathrm{kJ\ mol^{-1}}$.

1pt for $\Delta G = \Delta H - T\Delta S$

1pt for discussion on ΔH

In addition, it is reasonable to assume that entropy change is basically determined by the change of amount of gaseous species (neglecting entropy contributions from liquids and solids):

$\Delta n_{gas} = \Delta n_{gas-products} - \Delta n_{g-reactants} = +3\ \mathrm{mol}$. Hence, $\Delta S > 0$. It means both enthalpy term and entropy term ($-T\Delta S$) contribute to a decrease of Gibbs energy. Thus, the reaction proceeds spontaneously.

1pt for discussion on $-T\Delta S$

1pt for discussion on the both terms

HW02-06 [10pt in total: (1) 2pt, (2) 4pt, (3) 4pt]

[HW02-06:#19-36]
(3) At a much higher temperature like 1000 K, do you think the direction of the spontaneous reaction can be changed from that at 298.15 K? Please give your answer with explanation in 100 words or less. Please assume at both temperatures, the system is maintained at const.-T const.-P (1 bar) conditions.

- ✓ [1pt] At 1000 K, H_2O should become a gas. Then, the chemical equation needs to be modified as:

$$2F_2(g) + \ 2H_2O(g) \rightarrow 4HF(g) + O_2(g)$$

- ✓ [1pt] Enthalpy of liquid is lower than that of gas (because the enthalpy is largely composed of chemical bonding), ΔH at 1000 K should be smaller than (at least comparable with) that of 300 K ($-520\ \mathrm{kJ\ mol^{-1}}$).
- ✓ [1pt] Regarding entropy term, $\Delta n_{gas} = \Delta n_{gas-products} - \Delta n_{g-reactants} = +1\ \mathrm{mol}$. Hence, $\Delta S > 0$ is still achieved.
- ✓ [1pt] It means both enthalpy term and entropy term ($-T\Delta S$) contribute to a decrease of Gibbs energy. Thus, the reaction proceeds spontaneously.

HW02-07 [9pt in total: (1) 2pt, (2) 3pt, (3) 4pt]

<evaluation elements for (1)>

- ✓ If you forget the unit, 0 pt. If any mistake, 0 pt.

[HW02-07]

(1) Calculate the value of $\Delta_r H$ (at 298.15 K and 1 bar) for the reaction described by

$$C_6H_{12}O_6(s, \alpha - D - \text{Glucose}) + 3O_2(g) \rightarrow 6H_2O(l) + 6CO(g)$$

Regarding the data for standard molar enthalpies of formation at 298.15 K, please refer to the database on:

http://courses.chem.indiana.edu/c360/documents/thermodynamicdata.pdf

<Standard molar enthalpy of formation at 298.15 K>

Compound	$C_6H_{12}O_6$ (s)	$O_2(g)$	$H_2O(l)$	$CO(g)$
$\Delta_f H°$ (kJ/mol)	-1273.3	0	-285.8	-110.5

$$\Delta_r H = \sum\nolimits_{\text{products}} \Delta_f H° - \sum\nolimits_{\text{reactants}} \Delta_f H°$$

$$= \{6 \times \Delta_f H°(H_2O, l) \ + 6 \times \Delta_f H°(CO, g)\} - \{\Delta_f H°(C_6H_{12}O_6, s) + 3 \times \Delta_f H°(O_2, g)\}$$

$$= \{6 \times (-285.8) \ + 6 \times (-110.5)\} - \{(-1273.3) + 3 \times (0)\}$$

$$= -1105 \text{ kJ/mol}$$

HW02-07 [9pt in total: (1) 2pt, (2) 3pt, (3) 4pt]

[HW02-07] $C_6H_{12}O_6(s, \alpha - D - \mathrm{Glucose}) + 3O_2(g) \rightarrow 6H_2O(l) + 6CO(g)$
(2) At constant temperature and constant pressure condition (298.15 K and 1 bar), please determine whether this reaction proceeds simultaneously or not.

As obtained in HW02-06, at const.-T const.-P condition,

$$\Delta G = \Delta H - T\Delta S$$

Then, in (1), ΔH was determined as$-1105\ \mathrm{kJ/mol}$.

1pt for ΔH discussion

In addition, it is reasonable to assume that entropy change is basically determined by the change of amount of gaseous species (neglecting entropy contributions from liquids and solids):

$\Delta n_{gas} = \Delta n_{gas-products} - \Delta n_{g-reactants} = +3\ \mathrm{mol}$. Hence, $\Delta S > 0.$

It means both enthalpy term and entropy term ($-T\Delta S$) contribute to a decrease of Gibbs energy. Thus, the reaction proceeds spontaneously.

1pt for $\Delta G = \Delta H - T\Delta S$ and discussion on the balance of the 2 terms

1pt for ΔS $(or\ \ -T\Delta S)$ discussion

HW02-07 [9pt in total: (1) 2pt, (2) 3pt, (3) 4pt]

[HW02-07] $C_6H_{12}O_6(s, \alpha - D - \text{Glucose}) + 3O_2(g) \rightarrow 6H_2O(l) + 6CO(g)$
(3) How much is the maximum non-PV work that can be taken out from this reaction at const.-T and const.-P condition (298.15 K and 1 bar).

Compound	$C_6H_{12}O_6$ (s)	$O_2(g)$	$H_2O(l)$	$CO(g)$
$\Delta_f H°$ (kJ/mol)	-1273.3	0	-285.8	-110.5
$S°$ (J/K/mol)	212	205.2	70.0	197.7

The maximum non-PV work that can be taken out from this reaction at const.-T and const.-P condition is equal to Gibbs energy difference **(*See lecture #11)**.

$$\Delta G = \Delta H - T\Delta S$$

Then, in (1), ΔH was determined as -1105 kJ/mol.

2pt for "ΔG is the maximum non-PV work" that can be taken out

$$\Delta S = \sum_{\text{products}} S° - \sum_{\text{reactants}} S°$$
$$= \{6 \times S°(H_2O, l) \ + 6 \times S°(CO, g)\} - \{S°(C_6H_{12}O_6, s) + 3 \times S°(O_2, g)\}$$
$$= \{6 \times (70.0) \ + 6 \times (197.7)\} - \{(212) + 3 \times (205.2)\} = 778.6 \text{ J/K/mol}$$

Then, $\Delta G = \Delta H - T\Delta S = -1105 - 298.15 \times \frac{778.6}{1000.0} = -1337$ kJ/mol.

Thus, the maximum non-PV work is 1337 kJ/mol.

2pt for the calculation (if no/wrong unit, 0 pt)

HW02-08 [6pt in total: (1) 2pt, (2) 2pt, (3) 2pt]

[HW02-08]
As a step to manufacture nuclear fuel (UO_2), we need to go through so-called "conversion" process from U_3O_8 (s) to UF_6 (g). If needed, you can use the database given in http://courses.chem.indiana.edu/c360/documents/thermodynamicdata.pdf

(1) Complete the following chemical equation by giving appropriate numerals to $\alpha, \beta, \gamma, \delta$.

$$\mathrm{U_3O_8(s) + \alpha\, H_2(g) + \beta\, F_2(g) + \gamma\, HF(g) \rightarrow 3UF_6(g) + \delta\, H_2O(l)}$$

*Sorry, but this problem you cannot solely determine α, β, γ. You can choose any values as you like, as far as they keep the mass conservation.

[O mass conservation] $\delta = 8$
[H mass conservation] $2\alpha + \gamma = 2\delta = 16$
[F mass conservation] $2\beta + \gamma = 18$

So, possible combinations of (α, β, γ) is $(8, 9, 0)$, $(7, 8, 2)$, $(6, 7, 4)$, $(5, 6, 6)$, $(4, 5, 8)$, $(3, 4, 10)$, $(2, 3, 12)$, $(1, 2, 14)$, $(0, 1, 16)$

HW02-08 [6pt in total: (1) 2pt, (2) 2pt, (3) 2pt]

[HW02-08]
(2) Calculate the $\Delta_r H$ (at 298.15 K and 1 bar) for this reaction.

$$U_3O_8(s) + \alpha\, H_2(g) + \beta\, F_2(g) + \gamma\, HF(g) \rightarrow 3UF_6(g) + 8\, H_2O(l)$$

Compound	$U_3O_8(s)$	$H_2(g)$	$F_2(g)$	$HF(g)$	$UF_6(g)$	$H_2O(l)$
$\Delta_f H°$ (kJ/mol)	-3574.8	0	0	-273.3	-2147.4	-285.8
$S°$ (J/K/mol)	282.6	130.7	202.8	173.8	377.9	70.0

$$\Delta_r H = \sum\nolimits_{\text{products}} \Delta_f H° - \sum\nolimits_{\text{reactants}} \Delta_f H°$$
$$= \{3 \times (-2147.4) \ + 8 \times (-285.8)\} - \{(-3574.8) + \alpha \times (0) + \beta \times (0) + \gamma \times (-273.3)\}$$
$$= -5302.6 + 273.3 \times \gamma\ [\mathrm{kJ/mol}]$$

γ	0	2	4	6	8
$\Delta_r H$ (kJ/mol)	-5154	-4607	-4061	-3514	-2967

γ	10	12	14	16
$\Delta_r H$ (kJ/mol)	-2421	-1874	-1328	-781

2pt for the calculation (if no/wrong unit, 0 pt)

(Appendix) How to evaluate $\Delta_f G°$

- ✓ As the same with standard molar enthalpy of formation, standard molar Gibbs energy of formation defined so that that of pure elemental substance at standard state has $\Delta_f G° = 0\ [\mathrm{kJ/mol}]$.

Compound	$U_3O_8(s)$	$H_2(g)$	$F_2(g)$	$HF(g)$	$UF_6(g)$	$H_2O(l)$
$\Delta_f H°$ (kJ/mol)	-3574.8	0	0	-273.3	-2147.4	-285.8
$S°$ (J/K/mol)	282.6	130.7	202.8	173.8	377.9	70.0
$\Delta_f G°$ (kJ/mol)	-3369.5	0	0	-275.4	-2063.7	-237.1

- ✓ For example, for $\mathrm{HF(g)}$, the chemical equation for its formation reaction is:

$$\frac{1}{2}\ \mathrm{H_2(g)} + \frac{1}{2}\ \mathrm{F_2(g)} \rightarrow +\ \mathrm{HF(g)}$$

where $\Delta_f H°(\mathrm{HF, g; 298.15\ K}) = -273.3\ \mathrm{kJ/mol}$

- ✓ Then, $\Delta_f G°(\mathrm{HF, g; 298.15\ K}) = \Delta_f H°(\mathrm{HF, g; 298.15\ K}) - T\Delta S°$

$$= -273.3 - 298.15 \times \frac{173.8 - 0.5 \times (130.7 + 202.8)}{1000}$$

$$= -275.4\ \mathrm{kJ/mol}$$

- ✓ Confirm that this value is equal to what is given in the database.

<Appendix> Endothermic or Exothermic

- ✓ If a heat (q) is needed to proceed a reaction, the reaction is regarded as an endothermic reaction. If a heat is generated from the system (and can be released to the surroundings), the reaction is regarded as an exothermic reaction.

- ✓ In the case of constant-P condition (quasi-static), as q is equal to ΔH, whether the reaction of endothermic or exothermic is determined by ΔH, not ΔG.
  - ✓ $\Delta H > 0$: endothermic
  - ✓ $\Delta H < 0$: exothermic.

HW02-08 [6pt in total: (1) 2pt, (2) 2pt, (3) 2pt]

[HW02-08] $U_3O_8(s) + \alpha\, H_2(g) + \beta\, F_2(g) + \gamma\, HF(g) \rightarrow 3UF_6(g) + 8\, H_2O(l)$
(3) This reaction is apparently exothermic. In this reaction at 298.15 K at 1 bar with 1 mol of U_3O_8 (s), please determine how much non-PV work must be added at least or can be taken out from the system at most?

2pt for the calculation (if no/wrong unit, 0 pt)

For this, we need to calculate the Gibbs energy change.

Compound	$U_3O_8(s)$	$H_2(g)$	$F_2(g)$	$HF(g)$	$UF_6(g)$	$H_2O(l)$
$\Delta_f G°$ (kJ/mol)	-3369.5	0	0	-275.4	-2063.7	-237.1

$$\Delta_r G = \sum\nolimits_{\text{products}} \Delta_f G° - \sum\nolimits_{\text{reactants}} \Delta_f G°$$
$$= \{3 \times (-2068.5) \ + 8 \times (-237.1)\} - \{(-3369.5) + \alpha \times (0) + \beta \times (0) + \gamma \times (-273.3)\}$$
$$= -4732.8 + 275.4 \times \gamma \ [\text{kJ/mol}]$$

γ	0	2	4	6	8
Maximum energy(kJ/mol)	4718	4168	3617	3066	2512

γ	10	12	14	16
Maximum energy(kJ/mol)	1964	1414	863	312

As $\Delta_r G$>0, 4168 kJ/mol (for γ=2) should be added as non-PV work to proceed this reaction at least.

HW02-09 [5pt in total]

[HW02-09] Calculate the reaction enthalpy for

$C(s, graphite) + \mathrm{H_2O(g)} \rightarrow \mathrm{CO(g)} + \mathrm{H_2(g)}$

at 1273 K and 1 bar. Assume that the following heat capacity equations are valid between 298 K and 1273 K at 1 bar.

$C_P^\circ[\mathrm{CO(g)}]/R = 3.23 + (8.38 \times 10^{-4}\mathrm{K^{-1}})T - (9.86 \times 10^{-8}\mathrm{K^{-2}})T^2$

$C_P^\circ[H_2(\mathrm{g})]/R = 3.50 + (1.01 \times 10^{-4}\mathrm{K^{-1}})T + (2.42 \times 10^{-7}\mathrm{K^{-2}})T^2$

$C_P^\circ[H_2\mathrm{O(g)}]/R = 3.65 + (1.16 \times 10^{-3}\mathrm{K^{-1}})T + (1.42 \times 10^{-7}\mathrm{K^{-2}})T^2$

$C_P^\circ[\mathrm{C(s, graphite)}]/R$
$= -0.637 + (7.05 \times 10^{-3}\mathrm{K^{-1}})T - (5.20 \times 10^{-6}\mathrm{K^{-2}})T^2 + (1.38 \times 10^{-9}\mathrm{K^{-3}})T^3$

The definition of const.-P heat capacity is: $C_P = \left(\frac{\partial H}{\partial T}\right)_P$

Note that heat capacity depends on temperature (differently from ideal gas) Hence, at const.-P condition, which is achieved in this HW02-09, we can calculate the enthalpy change induced by a temperature change:

$$\Delta\overline{H} = \int d\overline{H} = \int \overline{C_P}\, dT \quad \text{[const.-P]}$$

*Here we assume no phase transition occurs in the temperature range for the integral.

$$\Delta_\mathrm{r}\mathrm{H}(T_1) = \sum_{\text{products}} \left(\Delta_\mathrm{f}\mathrm{H}^\circ(T_0) + \int_{T_0}^{T_1} \overline{C_P} dT\right) - \sum_{\text{reactants}} \left(\Delta_\mathrm{f}\mathrm{H}^\circ(T_0) + \int_{T_0}^{T_1} \overline{C_P} dT\right)$$

2pt for this kind of expression of $\Delta_\mathrm{r}\mathrm{H}(T_1)$

HW02-09 [5pt in total]

[HW02-09]
Calculate the reaction enthalpy for
$\mathrm{C}(s, graphite) + \mathrm{H_2O(g)} \rightarrow \mathrm{CO(g)} + \mathrm{H_2(g)}$
at 1273 K and 1 bar. Assume that the following heat capacity equations are valid between 298 K and 1273 K at 1 bar.

$$C_P^\circ[\mathrm{CO(g)}]/R = 3.23 + (8.38 \times 10^{-4}\mathrm{K}^{-1})T - (9.86 \times 10^{-8}\mathrm{K}^{-2})T^2$$

$$C_P^\circ[H_2(\mathrm{g})]/R = 3.50 + (1.01 \times 10^{-4}\mathrm{K}^{-1})T + (2.42 \times 10^{-7}\mathrm{K}^{-2})T^2$$

$$C_P^\circ[H_2\mathrm{O(g)}]/R = 3.65 + (1.16 \times 10^{-3}\mathrm{K}^{-1})T + (1.42 \times 10^{-7}\mathrm{K}^{-2})T^2$$

$$C_P^\circ[\mathrm{C(s, graphite)}]/R = -0.637 + (7.05 \times 10^{-3}\mathrm{K}^{-1})T - (5.20 \times 10^{-6}\mathrm{K}^{-2})T^2 + (1.38 \times 10^{-9}\mathrm{K}^{-3})T^3$$

Compound	$\mathrm{C(s, graphite)}$	$\mathrm{H_2O(g)}$	$\mathrm{CO(g)}$	$\mathrm{H_2(g)}$
$\Delta_f H°$ (298.15 K) [kJ/mol]	0	-241.8	-110.5	0

$$\Delta_\mathrm{r}\mathrm{H}(1273) = \sum_{\mathrm{products}}\left(\Delta_\mathrm{f}\mathrm{H}°(298.15) + \int_{298.15}^{1273}\overline{C_P}dT\right) - \sum_{\mathrm{reactants}}\left(\Delta_\mathrm{f}\mathrm{H}°(298.15) + \int_{298.15}^{1273}\overline{C_P}dT\right)$$

$$= -110.5 - (-241.8) + \sum_{\mathrm{products}}\left(\int_{298.15}^{1273}\overline{C_P}dT\right) - \sum_{\mathrm{reactants}}\left(\int_{298.15}^{1273}\overline{C_P}dT\right)$$

$$= 131.3 + 5.67 = 137.0\ [\ \mathrm{kJ/mol}\ ]$$

3pt for the result. If not/wrong unit, 0 pt.

HW02-10 [9pt in total: (1) 4pt, (2) 2pt, (3) 3pt]

[HW02-10]
(1) Vaporization at the normal boiling point (T_{vap}) of a substance (the boiling point at 1 atm) can be regarded as a reversible process because the molar fractions of liquid and gas phases are arbitrary (=cannot be uniquely determined) and the change can be induced by an infinitesimal addition/removal of heat. Calculate the entropy change when two moles of water vaporize at 100.0ºC. The value of $\Delta_{vap}\bar{H}$ is 40.65 kJ mol^{-1}.

As vaporization can be regarded as reversible process, entropy change is defined as

$$\Delta_{vap}S = \int \frac{\delta q}{T} = \frac{q_{vap}}{T_{vap}}$$

2pt for $\Delta_{tra}\bar{S} = \frac{\Delta_{tra}\bar{H}}{T_{tra}}$

Then, at const.-P condition,

$$dH = dU + d(PV) = (\delta q - PdV) + (PdV + VdP) = \delta q + VdP = \delta q$$

Thus,

$$\Delta_{vap}\bar{S} = \int \frac{\delta q}{T} = \frac{\Delta_{vap}\bar{H}}{T_{vap}} = \frac{40.65\times 10^3}{373.15} = 108.9 \text{ [J/K/mol]}$$

As we need to evaluate $\Delta_{vap}S$ for 2 moles, the answer is 217.9 [J/K].

2pt for the result (if no/wrong unit, 0 pt).

HW02-10 [9pt in total: (1) 4pt, (2) 2pt, (3) 3pt]

[HW02-10]

(2) Melting at the normal melting point (T_{fus}) of a substance (the melting point at 1 atm) can be regarded as a reversible process, by the same reason with the boiling point. Calculate the change in entropy when two moles of water melt at 0 ° C. The value of $\Delta_{fus}\bar{H}$ is 6.01 kJ mol^{-1}.

(3) Please compare the result with the result of (1) and (2), and discuss the reason of large difference in results in 100 words or less.

(2) As the same with (1),

$$\Delta_{melt}\bar{S} = \int \frac{\delta q}{T} = \frac{\Delta_{melt}\bar{H}}{T_{melt}} = \frac{6.01\times 10^3}{273.15} = 22.0 \text{ [J/K/mol]}$$

As we need to evaluate $\Delta_{melt}S$ for 2 moles, the answer is 44.0 [J/K].

2pt for the result (if no/wrong unit, 0 pt).

(3)

- ✓ [1pt] Entropy is an index for disorder.
- ✓ [1pt] In comparison between liquid and solid, the former is disordered more than the latter, but not so significantly different. On the other hand, in comparison between gas and liquid, the former is much more disordered.
- ✓ [1pt] Thus, in general, the following tendency is achieved: $S(g) \gg S(l) > S(s)$. Accordingly, $\Delta_{vap}S = \left(S(g) - S(l)\right) > \left(S(l) - S(s)\right) = \Delta_{melt}S$.

HW02-11 [6pt in total: (1) 4pt, (2) 2pt]

[HW02-11]
(1) The molar heat capacity of $H_2O(l)$ has an approximately constant value of $\overline{C_P}$=75.4 J K^{-1} mol^{-1} from 273 K to 373 K. Calculate ΔS if two moles of $H_2O(l)$ are heated from 273 K to 363 K at a constant pressure.
(2) The molar heat capacity of CO_2 at 1 bar can be expressed by
$\overline{C_P}/R = 3.23 + (8.38 \times 10^{-4}\mathrm{K}^{-1})T - (9.86 \times 10^{-8}\mathrm{K}^{-2})T^2$
over the temperature range $800\ K \leq T \leq 1300\ K$. Calculate ΔS if three moles of CO_2 is heated from 900 K to 1200 K at a constant pressure (1 bar).

(1) Due to const.-P condition, $dH = TdS + VdP = TdS$

Then, using the definition of $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ with assuming const.-P condition,

$$dH = C_P dT = TdS \qquad \text{[const.-P condition]}$$

Therefore, $\Delta S = \int dS = \int \frac{C_P}{T} dT$ *[const.-P condition]*

2pt for
$\Delta S = \int \frac{C_P}{T} dT$

Applying the given data into this equation,

$$\Delta S = \int \frac{C_P}{T} dT = 2 \times 75.4 \times \int \frac{dT}{T} = 150.8 \times \ln\left(\frac{363}{273}\right) = 43.0 \text{ [J/k]}$$

2pt for the result (if no/wrong unit, 0 pt).

(2) Likewise, $\Delta S = \int \frac{C_P}{T} dT = 3R \times \int \frac{\overline{C_P}}{T} dT = 3R \times 1.15 = 28.7$ [J/K]

2pt for the result (if no/wrong unit, 0 pt).

HW02-12 [5pt in total]

[HW02-12] The standard molar heat capacity of solid, liquid, and gaseous chlorine at 1 bar can be expressed as

$[15.0\ K \leq T \leq 172.12\ K]$

$C_P^\circ[Cl_2(\mathrm{s})]/R = -1.55 + (0.150\ \mathrm{K}^{-1})T - (1.18 \times 10^{-3}\mathrm{K}^{-2})T^2 + (3.44 \times 10^{-6}\mathrm{K}^{-3})T^3$

$[172.12\ K \leq T \leq 239.0\ K]$

$C_P^\circ[Cl_2(\mathrm{l})]/R = 7.69 + (5.58 \times 10^{-3}\ \mathrm{K}^{-1})T - (1.95 \times 10^{-5}\mathrm{K}^{-2})T^2$

$[239.0\ K \leq T \leq 1000\ K]$

$C_P^\circ[Cl_2(g)]/R = 3.81 + (1.22 \times 10^{-3}\ \mathrm{K}^{-1})T - (4.86 \times 10^{-7}\mathrm{K}^{-2})T^2$

At 15.0 K, the standard molar entropy of Cl_2(s) is given as 1.400 J K^{-1} mol^{-1}. Using these heat capacities data, and T_{fus}=172.12 K, $\Delta_{fus}\overline{H}$=6.41 kJ mol^{-1}, T_{vap}=239.0 K and $\Delta_{vap}\overline{H}$=20.4 kJ mol^{-1} at 1 bar, and the correction for non-ideality =0.502 J K^{-1} mol^{-1}, please calculate the standard molar entropy of chlorine at 400 K at 1 bar. (*Hint: regarding the correction for non-ideality, please just simply add it up.)

Combining the equations used in HW02-10 and HW02-11,

$$\bar{S}(400\ K)$$

$$= \bar{S}(15.0\ K) + \int_{15.0}^{172.12} \frac{\overline{C_P}}{T} dT + \frac{\Delta_{fus}\overline{H}}{172.12} + \int_{172.12}^{239.0} \frac{\overline{C_P}}{T} dT + \frac{\Delta_{vap}\overline{H}}{239.0} + \int_{239.0}^{400} \frac{\overline{C_P}}{T} dT + [non.id.]$$

$$= 1.400 + 68.8 + 37.2 + 21.9 + 85.4 + 17.7 + 0.502 = 232.9$$

= 233 [J/K/mol]

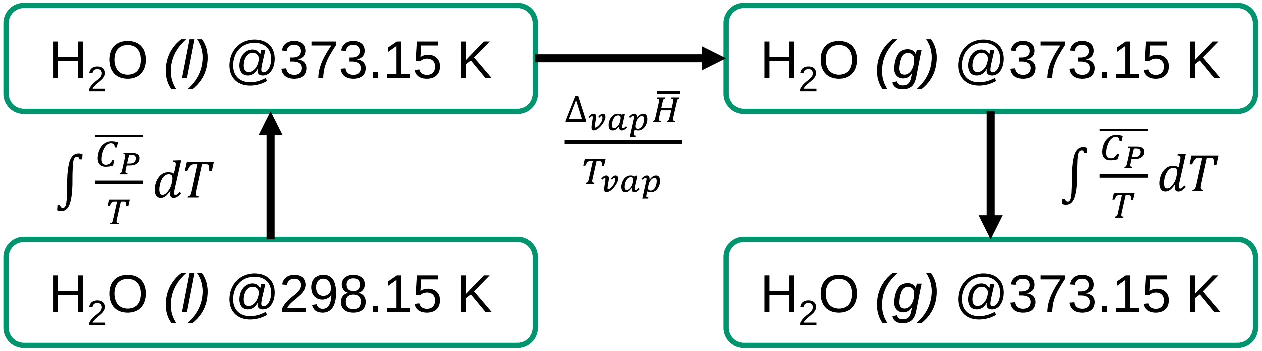
3pt for the expression

2pt for the result (if no/wrong unit, 0 pt).

HW02-13 [5pt in total]

[HW02-13:#21-46*] Calculate the value of $\bar{S}^{\circ}[H_2O(\mathrm{g})]$ at 298.15 K at 1 bar using the following data: $\bar{S}^{\circ}[H_2O(\mathrm{l})]$ =70.0 J K^{-1} mol^{-1} at 298.15 K, T_{vap}=373.15 K, $\Delta_{vap}\bar{H}$=40.7 kJ mol^{-1}, and $\overline{C_P}[H_2O(\mathrm{l})]$=75.3 J K^{-1} mol^{-1} and $\overline{C_P}[H_2O(\mathrm{g})]$=33.8 J K^{-1} mol^{-1} over 298.15-373.15 K at 1 bar.

Because const.-P condition is given, the answer is obtained by summing up the entropy changes in the following processes.



H_2O *(l)* @373.15 K

H_2O *(g)* @373.15 K

$\int \frac{\overline{C_P}}{T} dT$

$\frac{\Delta_{vap}\bar{H}}{T_{vap}}$

$\int \frac{\overline{C_P}}{T} dT$

H_2O *(l)* @298.15 K

H_2O *(g)* @373.15 K

$$\bar{S}^{\circ}[H_2O(\mathrm{g})] = \bar{S}^{\circ}[H_2O(\mathrm{l})] + \int_{298.15}^{373.15} \frac{\overline{C_{P,l}}}{T} dT + \frac{\Delta_{vap}\bar{H}}{T_{vap}} + \int_{373.15}^{298.15} \frac{\overline{C_{P,g}}}{T} dT$$

$= 70.0 + 16.90 + 109.1 - 7.584 = 188.4$ [J/K/mol]

*The experimental value is 188.8 [J/K/mol] according to the database.

3pt for the expression
2pt for the result (if no/wrong unit, 0 pt).

HW02-14 [5pt in total]

[HW02-14]
Arrange the following reactions to increasing values of $\Delta_r S^{\circ}$, according to typical differences of entropy among gas, liquid and solid states, with some explanation in 150 words or less. (*please do not check a database to evaluate the exact value of entropy)

a) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
b) $NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$
c) $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$
d) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
e) $NH_4Cl(l) \rightarrow NH_3(g) + HCl(g)$
f) $4CO(g) + 2O_2(g) \rightarrow 4CO_2(g)$

Following the given assumption (neglecting contribution from liquids and solids, relying on "$S^{\circ}(g) \gg S^{\circ}(l) > S^{\circ}(s)$"), we only check the change of gas amount by each reaction:

a) $\Delta n_{gas} = 0 - (2+1) = -3$
b) $\Delta n_{gas} = (1+1) - 0 = 2$
c) $\Delta n_{gas} = 2 - (2+1) = -1$
d) $\Delta n_{gas} = 2 - (2+1) = -1$
e) $\Delta n_{gas} = (1+1) - 0 = 2$
f) $\Delta n_{gas} = 4 - (2+4) = -2$

Regarding the comparison between c) and d), it is difficult to judge it because the structures of molecules involved in these reactions are similar.

Regarding the comparison between b) and e), $\Delta_r S^{\circ}$ of b) should be larger than $\Delta_r S^{\circ}$ of e), because the difference is liquid or solid of NH_4Cl and $S^{\circ}(l) > S^{\circ}(s)$.

Then, the answer is "a, f, (c~d), e, b" (or "a < f < c~d < e < b")

3pt for the answer
2pt for the discussion between b and e.

(Appendix) Comparison with the exact values.

H_2(g)	130.6 J/mol/K
O2 (g)	205.0
NH4Cl(s)	94.6
NH3 (g)	191.5
HCl(g)	186.8
H2O(g)	188.7
H2O(l)	69.9
CO(g)	197.6
CO2(g)	213.6
Ar(g)	154.8
He(g)	126.1

http://www.mrbigler.com/misc/energy-of-formation.PDF

If we exactly calculate the entropy change by the reaction, we achieve a) -396.3 [J/mol/K], b) 283.7, c) -88.8, d) 8.6, e) <283.7. f) -346. Then, the order is a<f<c<d<e<b.

This reasonably agrees with the solution:
a < f < c~d < e < b. However, if we look at details, there are some discrepancy, such as c~d. And the difference between a and f is also small.
So, this kind of concept is for just rough estimation based on a basic character of entropy (S_{gas}>>S_{liq}>S_{sol}, but the difference between gas and liquid is not so large indeed), and cannot give correct results always. However, the order is often reasonably given qualitatively.

I gave this problem to confirm whether you understand the basic character of entropy.

HW02-15 [6pt in total: (1) 3pt, (2) 3pt]

[HW02-15]
(1) Please derive the following equation: $(\partial \bar{G}/\partial P)_T = \bar{V}$
(2) Then, please draw a general P-$\bar{G}$ diagram at a temperature (constant) around the boiling point. (Please show 2 lines corresponding to $\bar{G}$ for gas and $\bar{G}$ for liquid. And use x-axis for P and y-axis for $\bar{G}$)

(1) For equilibrium states (or reversible processes)

$$dG = dH - d(TS) = \left(dU + d(PV)\right) - (TdS + SdT)$$
$$= (TdS - PdV + PdV + VdP) - (TdS + SdT) = VdP - SdT$$

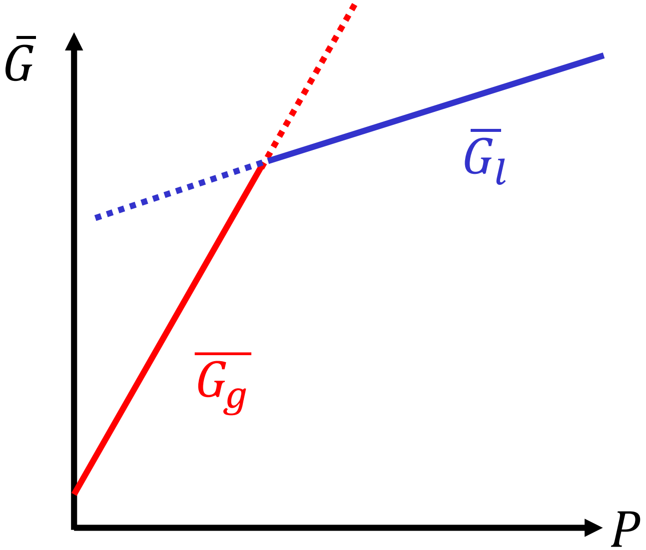
Taking partial derivative of P with fixing T:

$$\left(\frac{\partial G}{\partial P}\right)_T = V\left(\frac{\partial P}{\partial P}\right)_T - 0 = V \quad \text{then,} \quad \left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$$

3pt for (1)

(2) The key points of this figure are:

- ✓ $\left(\frac{\partial \bar{G}}{\partial P}\right)_T$ is always positive as it is equal to $\bar{V} > 0$.
- ✓ The slope, which is equal to $\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$, is steeper for gas than liquid, because $\bar{V}_g \gg \bar{V}_l$



3pt for figure. If missing key points, 0pt.
- ✓ If no/missing titles (axes and lines), -1pt.
- ✓ If not described by like dotted line, -1pt.

HW02-16 [6pt in total: (1) 3pt, (2) 3pt]

[HW02-16]
(1) Please derive the following equation: $(\partial \bar{G}/\partial T)_P = -\bar{S}$
(2) Then, please draw a general T-$\bar{G}$ diagram at a usual pressure around the boiling point. (Please show 2 lines corresponding to $\bar{G}$ for gas and $\bar{G}$ for liquid. And use x-axis for T and y-axis for $\bar{G}$)

(1) For equilibrium states (or reversible processes)

$$dG = VdP - SdT$$

Taking partial derivative of T with fixing P:

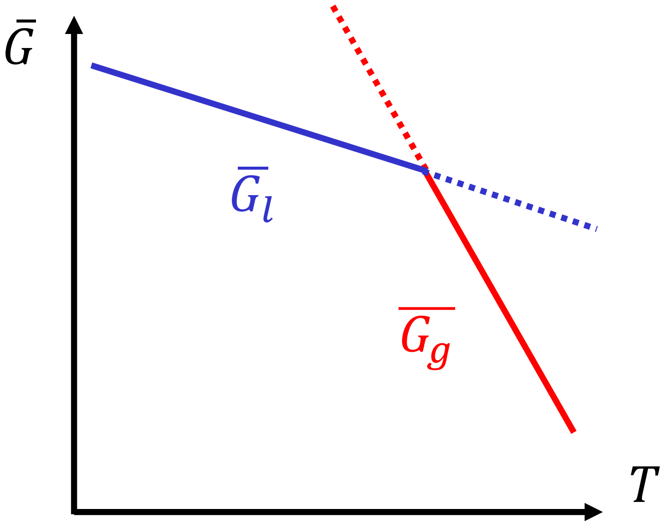
$$\left(\frac{\partial G}{\partial T}\right)_P = 0 - S = -S \quad \text{then,} \quad \left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}$$

3pt for (1)

(2) The key points of this figure are:

- ✓ $\left(\frac{\partial \bar{G}}{\partial T}\right)_P$ is always negative as it is equal to $-\bar{S} < 0$.
- ✓ The slope, which is equal to $\left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}$, is steeper (as negative slope) for gas than liquid, because $\bar{S}_g \gg \bar{S}_l$

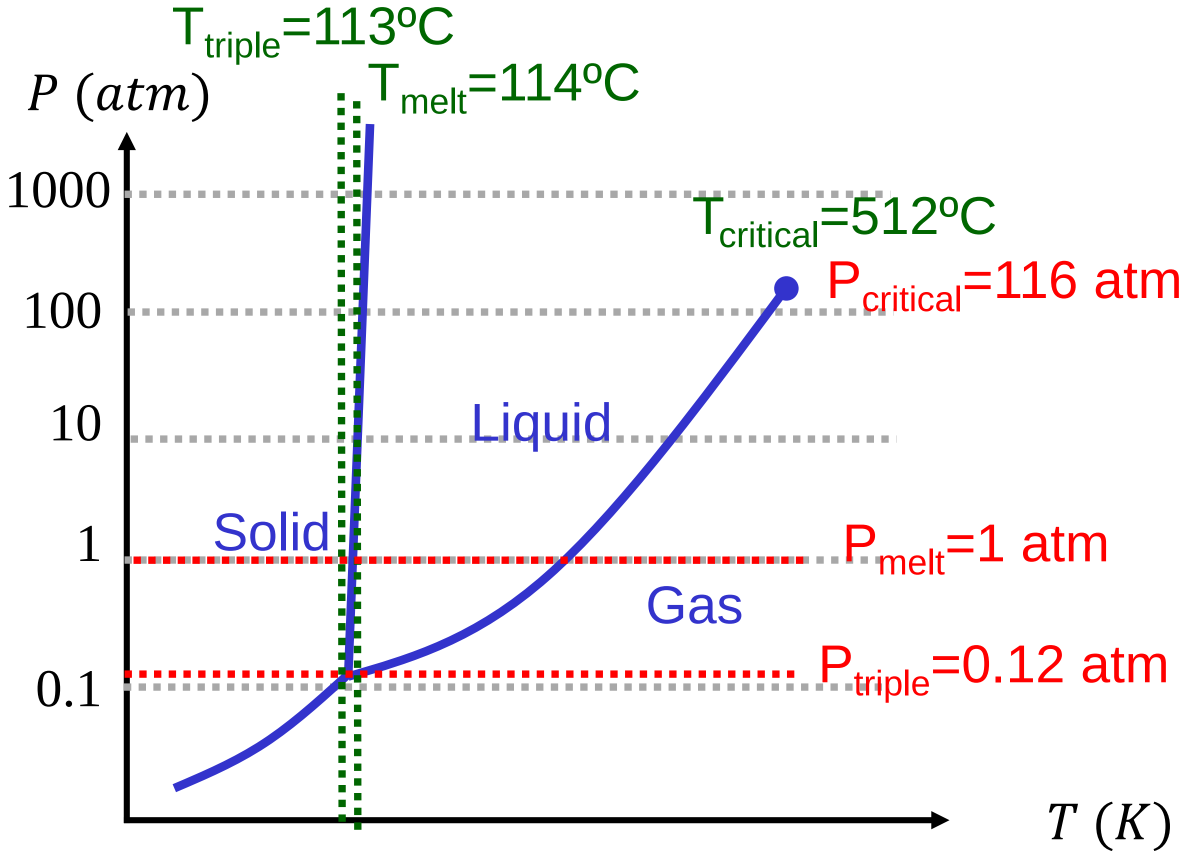
3pt for figure. If missing key points, 0pt.
- ✓ If no/missing titles (axes and lines), -1pt.
- ✓ If not described by like dotted line, -1pt.



HW02-17 [5pt in total]

[HW02-17: #23-2]

Sketch the phase diagram for I_2 using the following data: triple point at 113ºC and 0.12 atm; critical point at 512ºC and 116 atm; normal melting point at 114ºC; and normal boiling point at 184ºC. The x-axis should be temperature over 300-800 K, the y-axis should be pressure in atm unit (common logarithms).



The key points of this figure is:

- ✓ Clear description of key pressures and temperatures.
- ✓ Clear description of each phases and axes.
- ✓ The definition of normal melting point (P=1atm).
- ✓ [2pt] The shape of coexistence curves, especially L-S and G-S.

HW02-18 [9 pt in total: (1) 3pt, (2) 6pt]

[HW02-18: #23-22] (1) Please derive the *Clapeyron equation, namely*

$$\frac{dP}{dT} = \frac{\Delta_{trs}\bar{H}}{T\Delta_{trs}\bar{V}}$$

Considering 2 phases are of equilibrium each other (α and β phases), their chemical potential must be equal each other.

$$\mu^{\alpha}(T,P) = \mu^{\beta}(T,P)$$

Now take the total derivatives o both sides

$$\left(\frac{\partial\mu^{\alpha}}{\partial P}\right)_T dP + \left(\frac{\partial\mu^{\alpha}}{\partial T}\right)_P dT = \left(\frac{\partial\mu^{\beta}}{\partial P}\right)_T dP + \left(\frac{\partial\mu^{\beta}}{\partial T}\right)_P dT$$

Since μ is simply the molar Gibbs energy for a single substance, utilizing $\left(\frac{\partial G}{\partial P}\right)_T = V$ and $\left(\frac{\partial G}{\partial T}\right)_P = -S$ (*these were previously derived along Maxwell relations)

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

where $\bar{V}$ and $\bar{S}$ are the molar volume and the molar entropy. Then,

$$\bar{V}^{\alpha}dP - \bar{S}^{\alpha}dT = \bar{V}^{\beta}dP - \bar{S}^{\beta}dT$$

Since we consider the two phases are in equilibrium each other

$$\frac{dP}{dT} = \frac{\bar{S}^{\beta}-\bar{S}^{\alpha}}{\bar{V}^{\beta}-\bar{V}^{\alpha}} = \frac{\Delta_{trs}\bar{S}}{\Delta_{trs}\bar{V}} = \frac{\Delta_{trs}\bar{H}/T}{\Delta_{trs}\bar{V}} = \frac{\Delta_{trs}\bar{H}}{T\Delta_{trs}\bar{V}}$$

HW02-18 [9 pt in total: (1) 3pt, (2) 6pt]

[HW02-18: #23-22] (1) Please derive the *Clapeyron equation, namely* $\frac{dP}{dT} = \frac{\Delta_{trs}\overline{H}}{T\Delta_{trs}\overline{V}}$

(2) The vapor pressure of mercury from 400ºC to 1300ºC can be expressed by

$$\ln(P/torr) = -\frac{7060.7\ K}{T} + 17.85$$

The density of the vapor at its normal boiling point is 3.82 g L^{-1} and that of the liquid is 12.7 g cm^{-3}. Estimate the molar enthalpy of vaporization of mercury at its normal boiling point. The molar mass of mercury is 200.59 g mol^{-1}.

(2) First, we will determine the normal boiling temperature, where the gas pressure stands at 1 atm = 760 torr.

Thus, $\ln(760) = -\frac{7060.7}{T_{vap}} + 17.85$ then $T_{vap} = 629.5$ K .

Although this temperature is not in the rate of the equation (673~1573 K), as 629.5 K is close to the limit (673 K), we assume the error is limited.

2pt for the melting point

2pt for the discussion on the out-range

HW02-18 [9 pt in total: (1) 3pt, (2) 6pt]

[HW02-18: #23-22] (1) Please derive the *Clapeyron equation, namely* $\frac{dP}{dT} = \frac{\Delta_{trs}\bar{H}}{T\Delta_{trs}\bar{V}}$

(2) The vapor pressure of mercury from 400ºC to 1300ºC can be expressed by

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The density of the vapor at its normal boiling point is 3.82 g L^{-1} and that of the liquid is 12.7 g cm^{-3}. Estimate the molar enthalpy of vaporization of mercury at its normal boiling point. The molar mass of mercury is 200.59 g mol^{-1}.

(2) Next, take the derivative of pressure expression regarding T:

the pressure unit is converted to [Pa] from [Torr].

$$\frac{d\ln P}{dT} = \frac{1}{P}\frac{dP}{dT} = \frac{7060.7}{T^2}$$

Then,

$$\Delta_{vap}\bar{H} = T_{vap}\Delta_{vap}\bar{V} \times \frac{dP}{dT} = T_{vap}\Delta_{vap}\bar{V} \times \frac{7060.7}{{T_{vap}}^2}P_{vap} = \Delta_{vap}\bar{V} \times \frac{7060.7}{T_{vap}}P_{vap}$$

$$= \left(\frac{200.59}{3.82\times10^3} - \frac{200.59}{12.7\times10^6}\right) \times \frac{7060.7}{629.5} \times (1.013\times10^5) = 59.6\times10^3 \text{ [J/mol]}$$

$$= 59.6 \text{ [kJ/mol]}$$

2pt for the result (if no/wrong unit, 0 pt).

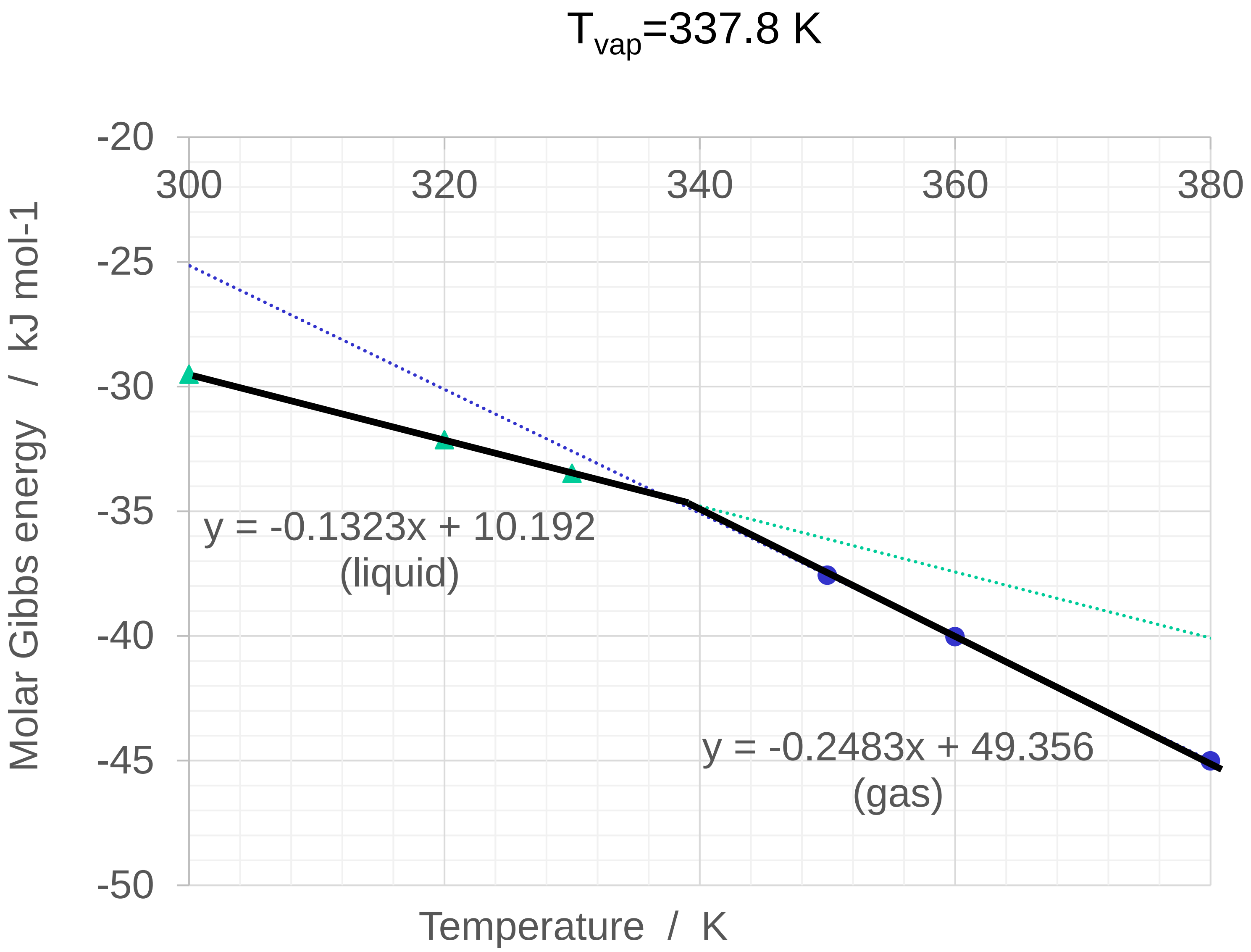
HW02-19 [8pt in total: 2 pt for each figure and 2 pt for T_{vap}]

[HW02-19: #23-17*] Using the following data for methanol at 1 atm, plot $\bar{G}(T\ K)$, $\bar{H}(T\ K, 1\ atm) - \bar{H}(T_{melt}\ K, 1\ atm)$, and $\bar{S}(T\ K, 1\ atm)$, against T over 300-380 K at 1 atm. Then, determine the normal melting point (the melting point at 1 atm) of methanol. Please assume that $\bar{G}, \bar{H}$ and $\bar{S}$ are proportional to temperature on this temperature range (300-380 K) for both liquid and gas, unless a phase transition is involved.

Temperature (K)	$\bar{H}(T\ K, 1\ atm) - \bar{H}(T_{melt}\ K, 1\ atm)$ / **kJ mol^{-1}**	$\bar{S}(T\ K, 1\ atm)$ / **J mol^{-1} K^{-1}**
300 [liquid]	9.301	129.4
320 [liquid]	10.99	134.8
330 [liquid]	11.87	137.4
350 [gas]	48.51	245.9
360 [gas]	49.06	247.5
380 [gas]	50.15	250.4

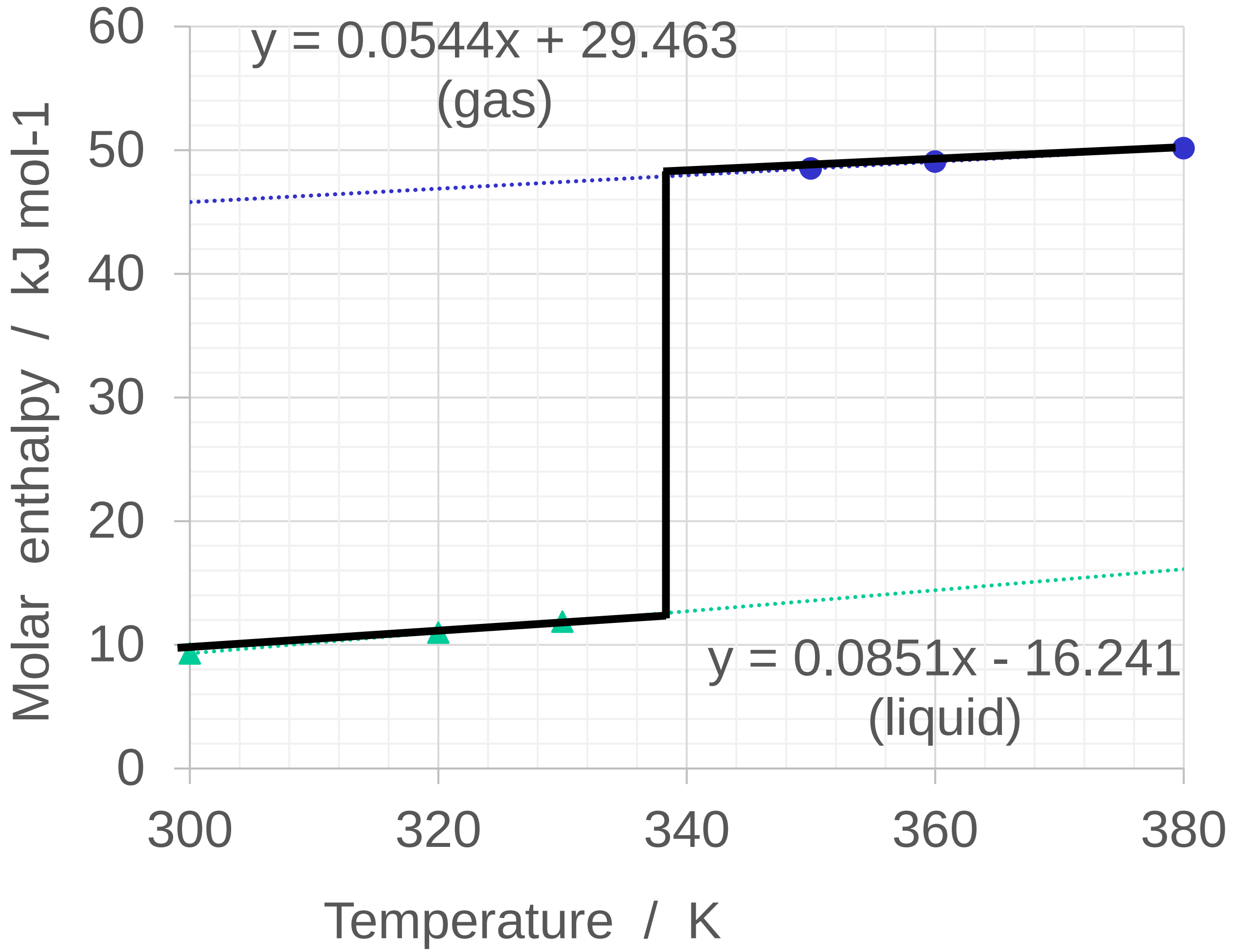
Here, $\bar{H}(T\ K, 1\ atm)$ and $\bar{S}(T\ K, 1\ atm)$ are molar enthalpy and molar entropy for $T\ K$ and $1\ atm$, respectively. The molar entropy is given with an absolute value. $\bar{G}(T\ K)$ is defined as: $\bar{G}(T\ K) = \bar{H}(T\ K, 1\ atm) - \bar{H}(T_{melt}\ K, 1\ atm) - T\bar{S}(T\ K, 1\ atm)$

HW02-19 [8pt in total: 2 pt for each figure and 2 pt for T_{vap}]

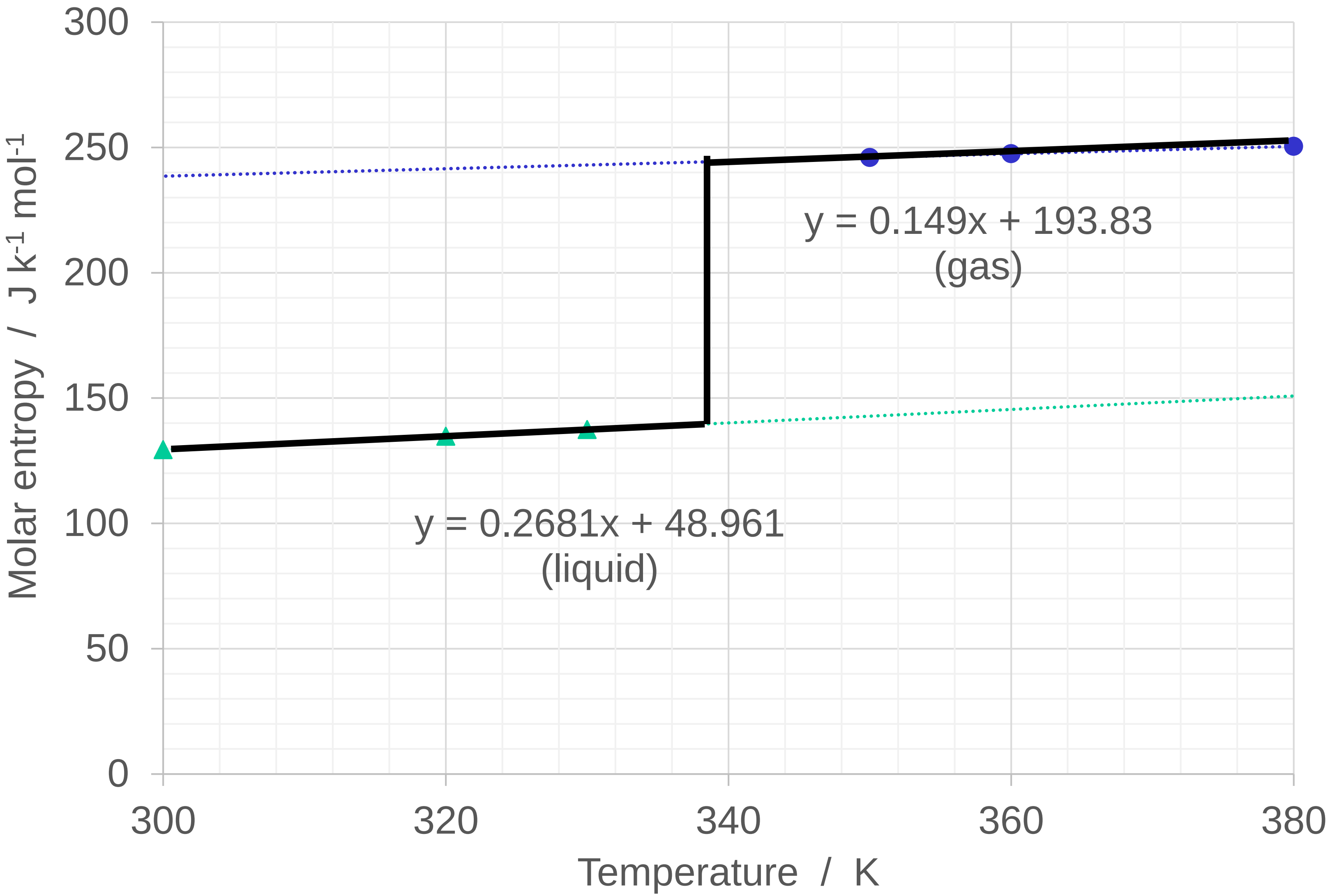


T_{vap}=337.8 K

HW02-19 [8pt in total: 2 pt for each figure and 2 pt for T_{vap}]



HW02-19 [8pt in total: 2 pt for each figure and 2 pt for T_{vap}]



HW02-19:

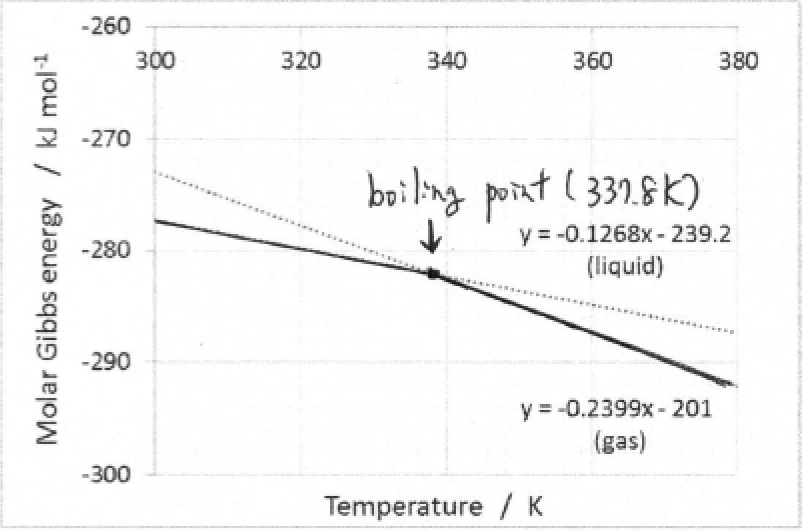
At boiling point

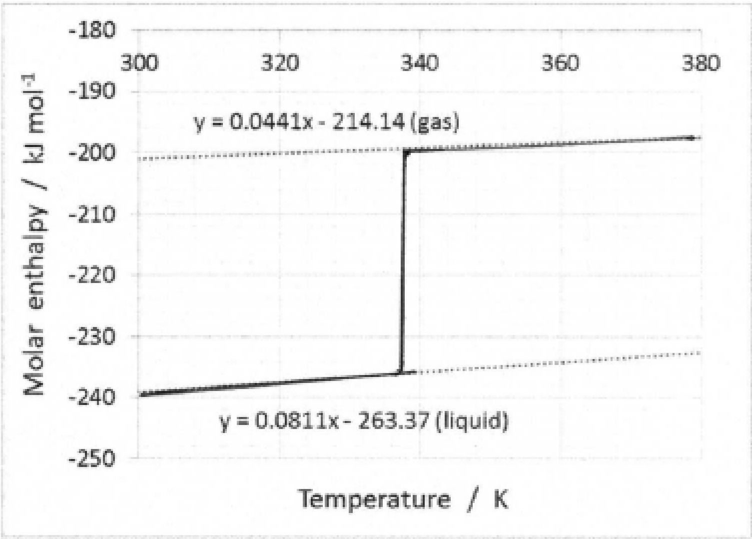
$$\bar{G}^{liquid} = \bar{G}^{gas}$$

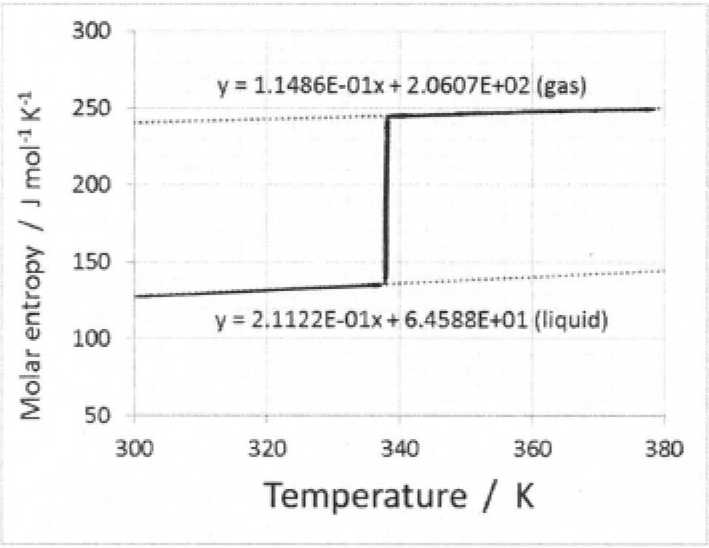
Thus,

$$T_{vap} = \frac{239.2 - 201.0}{(239.9 - 126.8)\times 10^{-3}}$$

$$= 337.8 \text{ K} \quad //$$







HW02-20 [5pt]

<evaluation elements>
- ✓ If you use a word-processor (software as well), -3 pt.

[HW02-20] Please explain why the degree of freedom (of intensive properties) can be given as “$f=c-p+2$, where c is the number of components, p is the number of phase that coexist at equilibrium at that point”, namely Gibbs’ phase rule.

The phase rule is write as:

$$f = \underbrace{2}_{(1)} + \underbrace{(c-1)p}_{(2)} - \underbrace{(p-1)c}_{(3)} = c - p + 2$$

- ✓ (1) the equilibrium of multiple phase is determined by chemical potential (molar Gibbs energy for const.-P and const.-T condition). And as chemical potential is intensive quantity (like $\mu = \mu(P,T)$), 2 quantities are enough to determine it. (*If extensive, 3 quantities are needed, e.g. n in addition)
- ✓ (2) if multiple component, we need to know how many amount is for each component for each phase. However, again, as chemical potential is intensive, we do not need to know the absolute amount: compositions (specified by “molar fraction”) are enough. The number of independent molar fractions is $(c-1)$ for each phase, then $(c-1)p$ for all.
- ✓ (3) This is due to the number of constraints in chemical potential for equilibrium states. The number of constraints is $(p-1)$ for each component, then $(p-1)c$ for all:

HW02-21 [6pt in total]

<evaluation elements>

- ✓ If you use a word-processor (software as well), -4 pt.

[HW02-21] Please derive “the mass transfer occurs from the phase of higher chemical potential to the phase of lower chemical potential at const.-T const.-P condition” for a system consisting of two phases of a pure substance (1-component) in equilibrium each other.

We consider a system consisting of two phases of a pure substance (1-component) in equilibrium each other. (liquid and gas, for example here)

The Gibbs energy of this system is given by

$$G = G^l + G^g$$

where G^l and G^g are the Gibbs energies of the liquid and the gas phase.

Now, suppose dn (infinitesimal amount) mole are transferred from the liquid to the solid phase, where T and P are kept constant. The infinitesimal change in Gibbs energy for this process is:

$$dG = dG^l + dG^g = \left(\frac{\partial G^g}{\partial n^g}\right)_{P,T} dn^g + \left(\frac{\partial G^g}{\partial P}\right)_{n^g,T} dP + \left(\frac{\partial G^g}{\partial T}\right)_{n^g,P} dT + \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T} dn^l + \left(\frac{\partial G^l}{\partial P}\right)_{n^l,T} dP + \left(\frac{\partial G^l}{\partial T}\right)_{n^l,P} = \left(\frac{\partial G^g}{\partial n^g}\right)_{P,T} dn^g + \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T} dn^l$$

HW02-21 [6pt in total]

[HW02-21] Please derive “the mass transfer occurs from the phase of higher chemical potential to the phase of lower chemical potential at const.-T const.-P condition” for a system consisting of two phases of a pure substance (1-component) in equilibrium each other.

As $dn^l = -dn^g$, then $dG = \left[\left(\frac{\partial G^g}{\partial n^g}\right)_{P,T} - \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T}\right] dn^g$

Here, we define *chemical potentials,* $\mu^g = \left(\frac{\partial G^g}{\partial n^g}\right)_{P,T}$ and $\mu^l = \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T}$, then

$dG = [\mu^g - \mu^l] dn^g$ (constant T and P)

3 pt for this derivation

- ✓ If the two phases are in equilibrium with each other, then $dG = 0$.
- ✓ And because we suppose some amount of the liquid phase is transferred to the gas phase (dn^g) here, to make $dG = 0$ in this condition, $\mu^g = \mu^l$ is needed.
  - ➢ If $\mu^g < \mu^l$, “$(\mu^g - \mu^l) < 0$’. Thus, the process of $dn^g > 0$ (transfer from the liquid phase to the gas phase) spontaneously takes place as it holds $dG < 0$.
  - ➢ Likewise, if $\mu^g > \mu^l$, $dn^g < 0$.
  - ➢ Hence, in general, the mass transfer occurs from the phase of higher chemical potential to the phase of lower chemical potential.

3 pt for this discussion

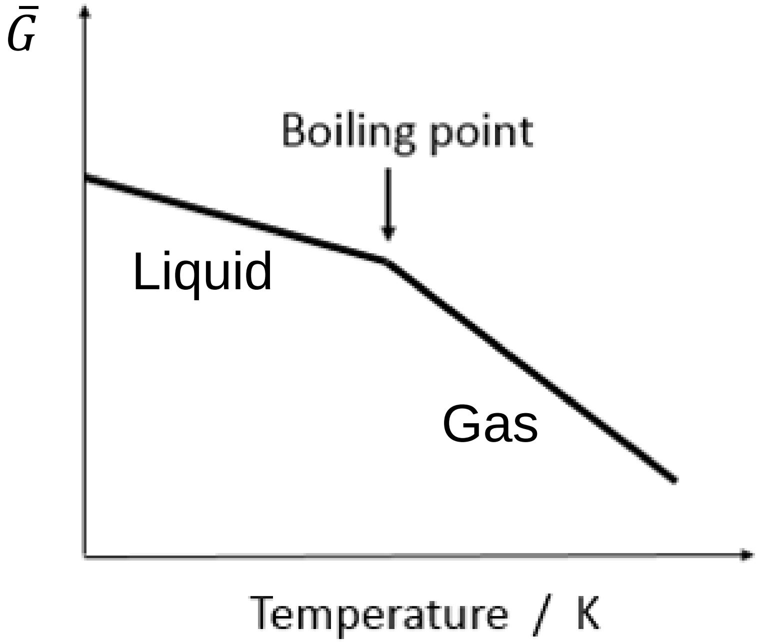
HW02-22 [8pt in total]

[HW02-22] Please draw a typical temperature dependence of the following thermodynamical quantities at around the boiling point at 1 bar for a general substance.
(1) molar Gibbs energy, (2) molar enthalpy, (3) molar entropy, (4) molar volume

<evaluation elements>

- ✓ 2pt for each
- ✓ If your figure miss even one of the multiple criteria, no point.
- ✓ If you do not write titles of x and y axes, -1 pt.

(1)

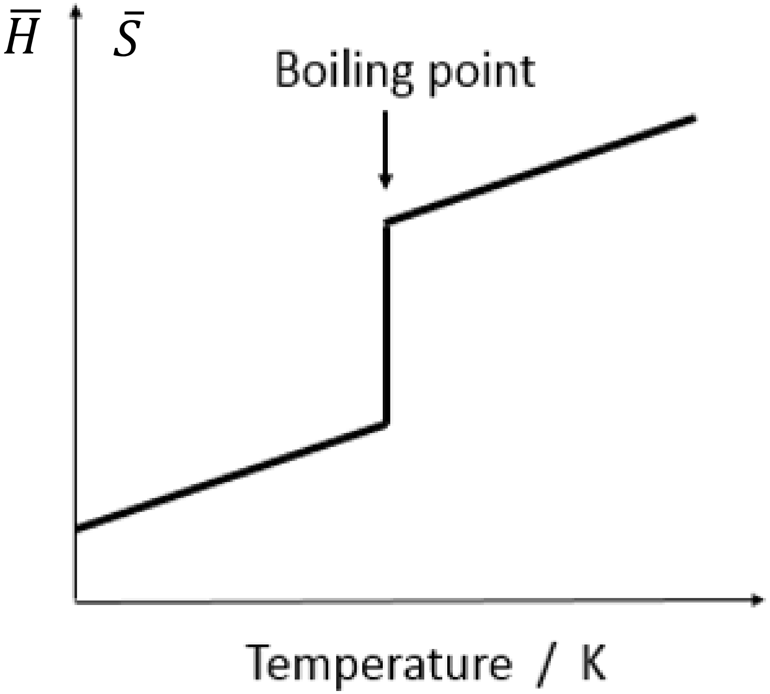


<Criteria>
(1) Continuity
(2) The phase holds a minimum Gibbs energy is the equilibrium phase
(3) For “$dG = -SdT + VdP$” and $dP = 0$, thus $dG/dT = -S < 0$.

In case there is a discontinuity….

HW02-22 [8pt in total]

[HW02-22]	(2) molar enthalpy	(3) molar entropy



<Basics>

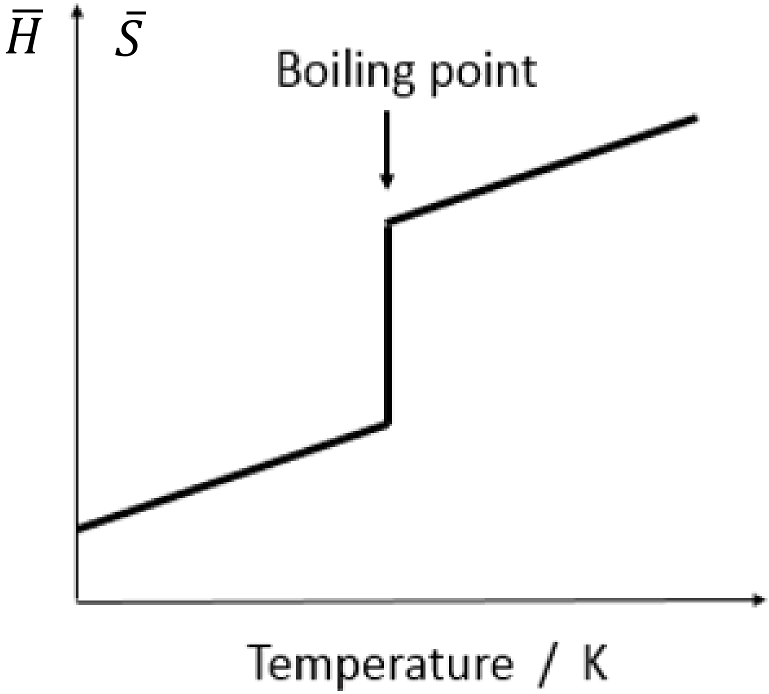
- ✓ H (and U) is largely composed by binding energy. Then, at higher temperatures, due to the thermal vibration, the binding energy decreases which means the energy increases.

  *Be careful H and U change in an opposite direction to the binding energy.

- ✓ S reflects the disorder of system. At higher temperatures, due to the thermal vibration, the system is more disordered.

HW02-22 [8pt in total]

[HW02-22] (2) molar enthalpy (3) molar entropy



<Criteria>

(1) Discontinuity at the phase transition (here, boiling point)

- ✓ The binding energy and the disorder degree largely change when the phase is changed. (e.g. solid to liquid) So, a gap appears.

(2) Gas holds a higher value than liquid, and liquid than solid.

- ✓ [H] The binding energy decrease from s to l and l to g, which means the energy increases.
- ✓ [S] The disorder degree increases from s to l and l to g.

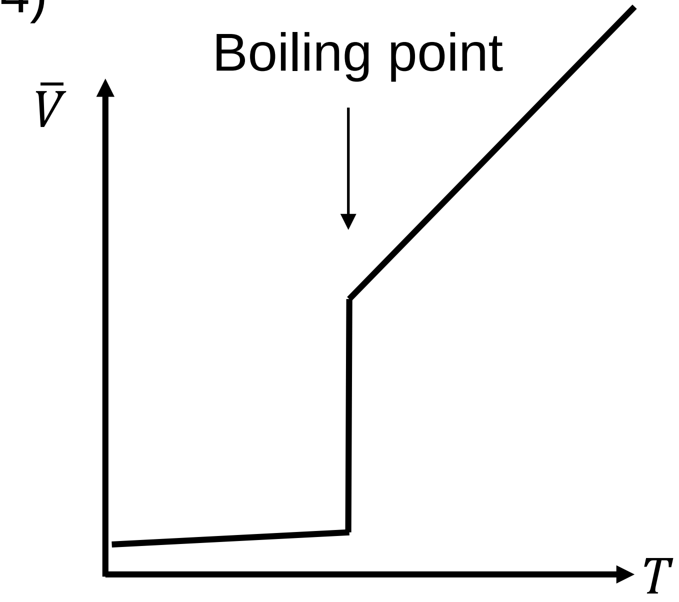
(3) The slope is positive (within one phase)

- ✓ [H] The binding energy decrease due to the thermal vibration at higher temperatures. which manes the energy increases
- ✓ [S] The disorder increases due to the thermal vibration at higher temperatures.

HW02-22 [8pt in total]

[HW02-22] (4) molar volume

(4)



<Criteria>

(1) The slope for gas should be much larger than that of liquid.

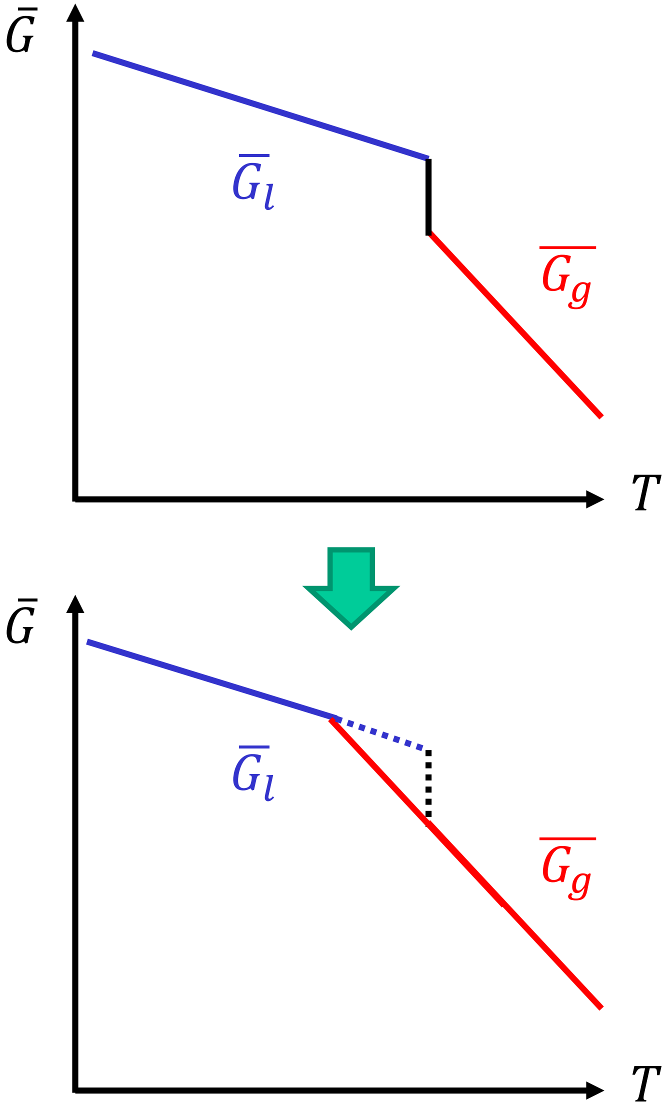
- ✓ The temperature dependence of (molar) volume is quite small for condensed phases (liquid and solid).
- ✓ Gas volume largely depends on temperature: e.g. for ideal gas, $PV = nRT$ and $P\bar{V} = RT$

(2) $\bar{V}$ for gas is much larger than $\bar{V}$ for liquid.

- ✓ In comparison between liquid and solid phase at around melting point, they are comparable, and the difference depends on material.

(Appendix) Why no discontinuity in Gibbs energy?

In the criteria in Gibbs energy graph, no discontinuity is listed. But why so?



- ✓ From the definition of Gibbs energy ($G = H - TS$), its behavior depends on H and S.
  - ✓ Both H and S hold (smooth) continuity within one phase (e.g. solid), because they reflect binding energy and system disorder.
  - ✓ Thus, G should also holds (smooth) continuity within one phase.

- ✓ On the other hand, at the condition of phase transition, both H and S present a discontinuity, while G does not. Why?
- ✓ If we have a discontinuity in G, we must find some phases having lower energy. So, the drawing is wrong.

(Quiz) At const.-T const.-V condition, does Gibbs energy may have a discontinuity?