Chemical Thermodynamics

Free Energy

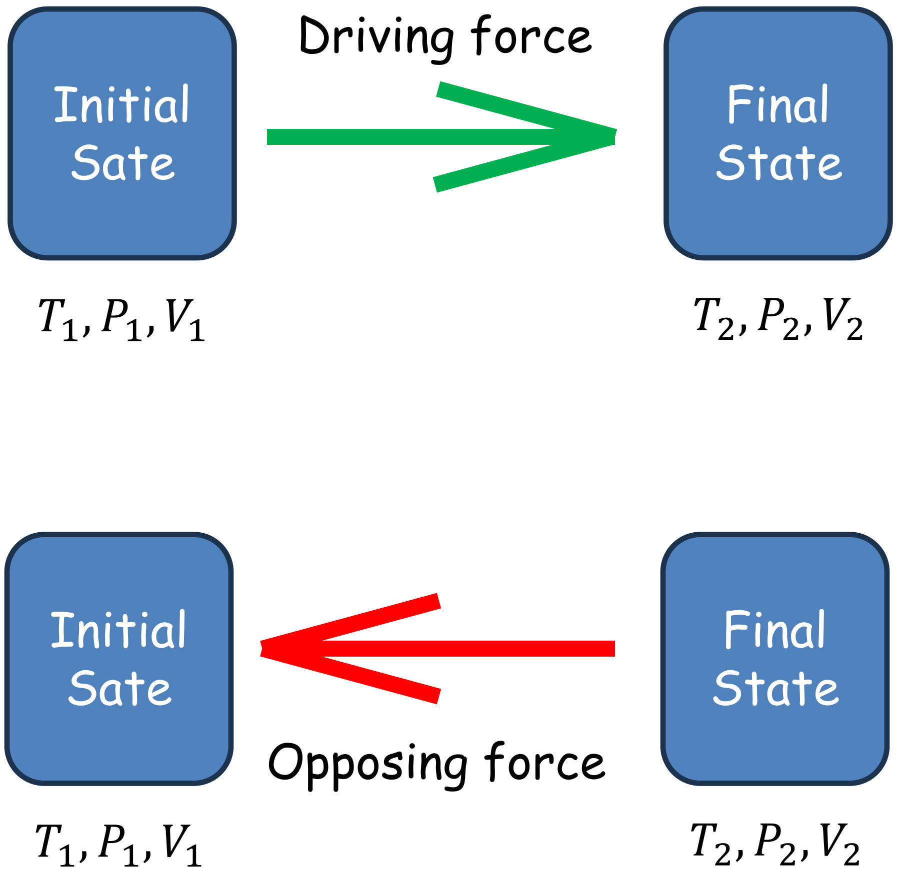
Recommended books

1. P. W. Atkins and J. D. Paula: Physical Chemistry (10th edition)
2. Ira N. Levine: Physical Chemistry (6th edition)
3. M. Mahbubul Huque and M. Yousuf Ali Mollah: Principles of Physical Chemistry

Free Energy

Spontaneity in terms of internal energy, enthalpy and entropy, Helmholtz and Gibbs energies, Gibbs-Helmholtz equation, free energy and spontaneity, thermodynamic equations of state, Gibbs equations, Maxwell relations, dependence of state functions on state variables, calculations of changes in state functions.

Fundamental Concepts



Initial Sate

Driving force

Final State

T_1, P_1, V_1

T_2, P_2, V_2

Initial Sate

Opposing force

Final State

T_1, P_1, V_1

T_2, P_2, V_2

Spontaneous Processes

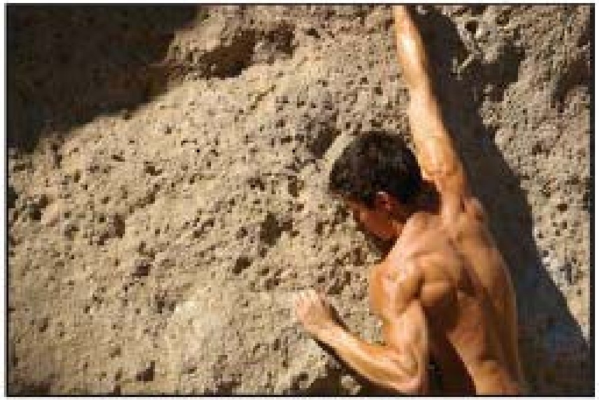
- Processes occur when there exist driving force for a change of state between the parts of the system or between the system and the surrounding.
- If the driving force is finite, the process is *irreversible*.
- If the driving force is infinitesimal in magnitude, the process is *reversible*.
- *Spontaneous* process is one that occurs its own accords without external intervention.

Fundamental Concepts

Examples of Spontaneous Processes

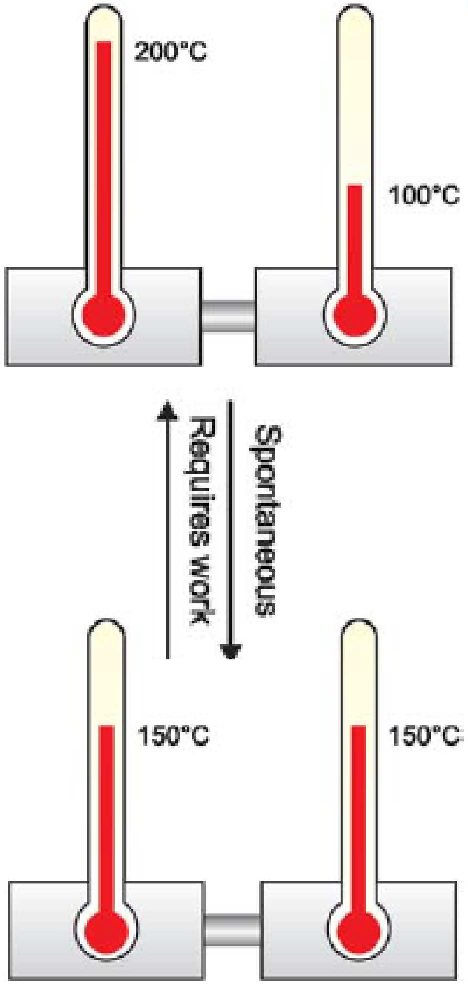
(a) Cliff Jumping and Mountain Climbing

Spontaneous

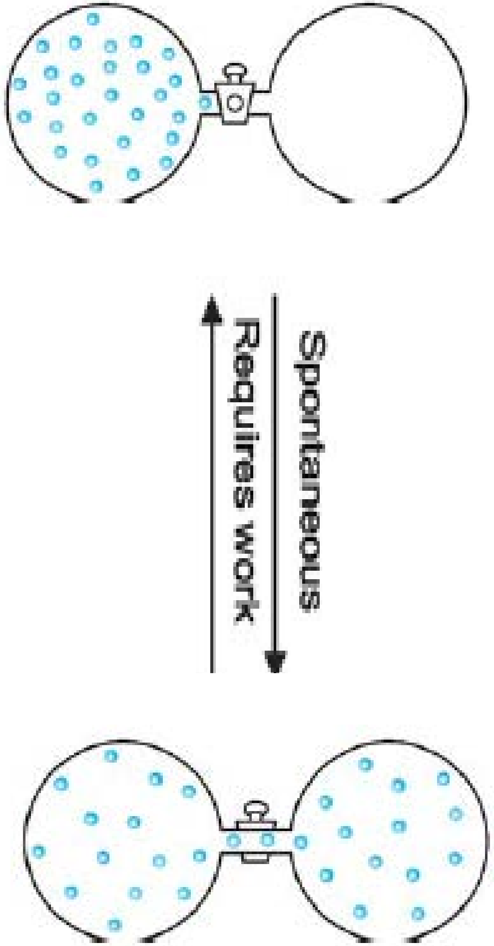


Requires work

(b) Heat Flow



(c) Gas Flow



Fundamental Concepts

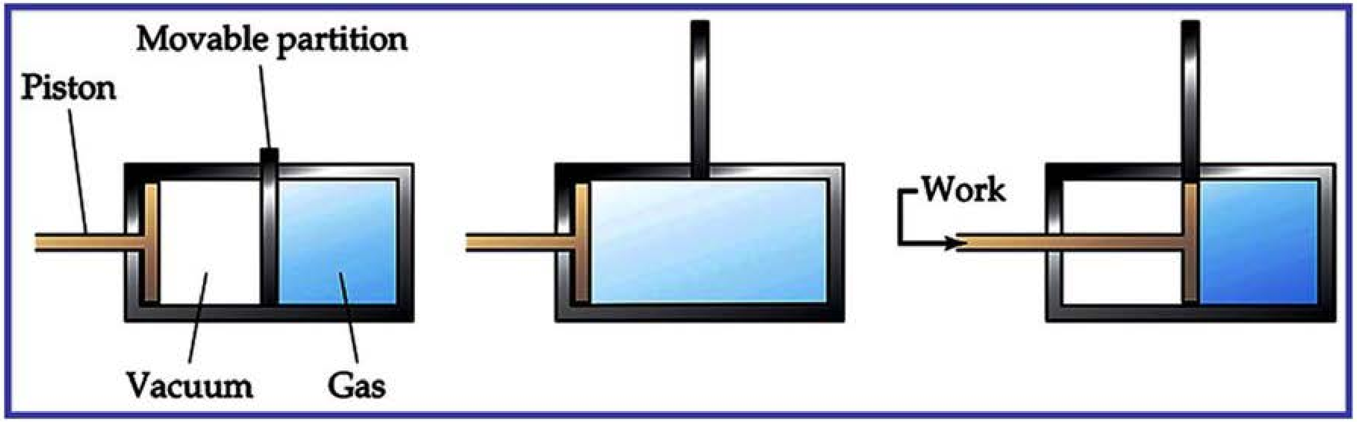
Examples of Spontaneous Processes

Fundamental Concepts

Irreversible processes

An **irreversible process** is one that cannot be reversed without leaving a net change in the system or its surroundings.

- In other words, when a process is irreversible, the system cannot return to its original state without external intervention or by adding extra energy.

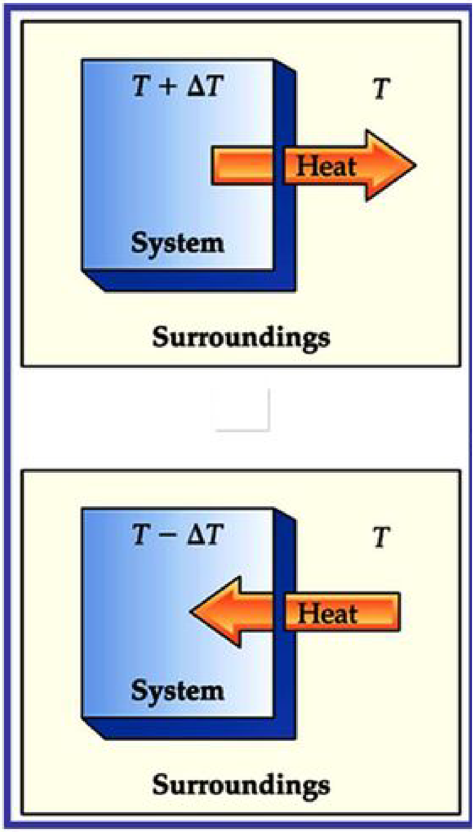


- Processes that cannot be undone by exactly reversing the process.
- All spontaneous processes are irreversible.
- All real processes are irreversible.

Fundamental Concepts

Reversible process (Idealizations!)

A **reversible process** in thermodynamics is an idealized process that occurs in such a way that the system and its surroundings can be returned to their original states by reversing the process without leaving any lasting changes.

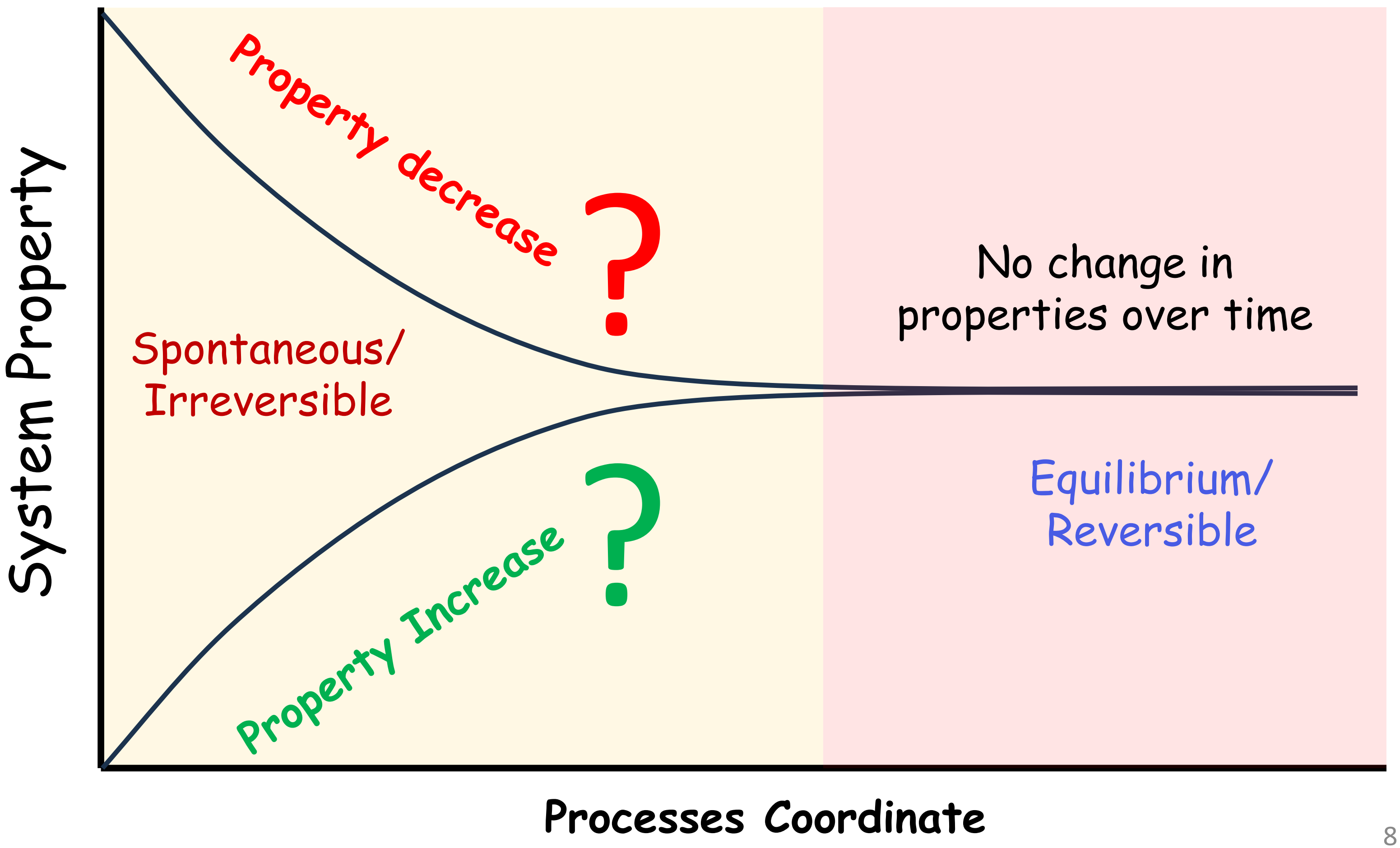


- In a reversible process, changes proceed in infinitesimally small steps, so that the system is infinitesimally close to equilibrium at every step.
- This is clearly an idealization and can never happen in a real system!
- Because of some unavoidable factors like friction, heat loss and finite process speeds
- The reversible conditions can be approximated in certain scenarios, such as
  - **Slowly compressed or expanded gases**
  - **Slow heat transfer**
  - **Electrochemical reactions in batteries**

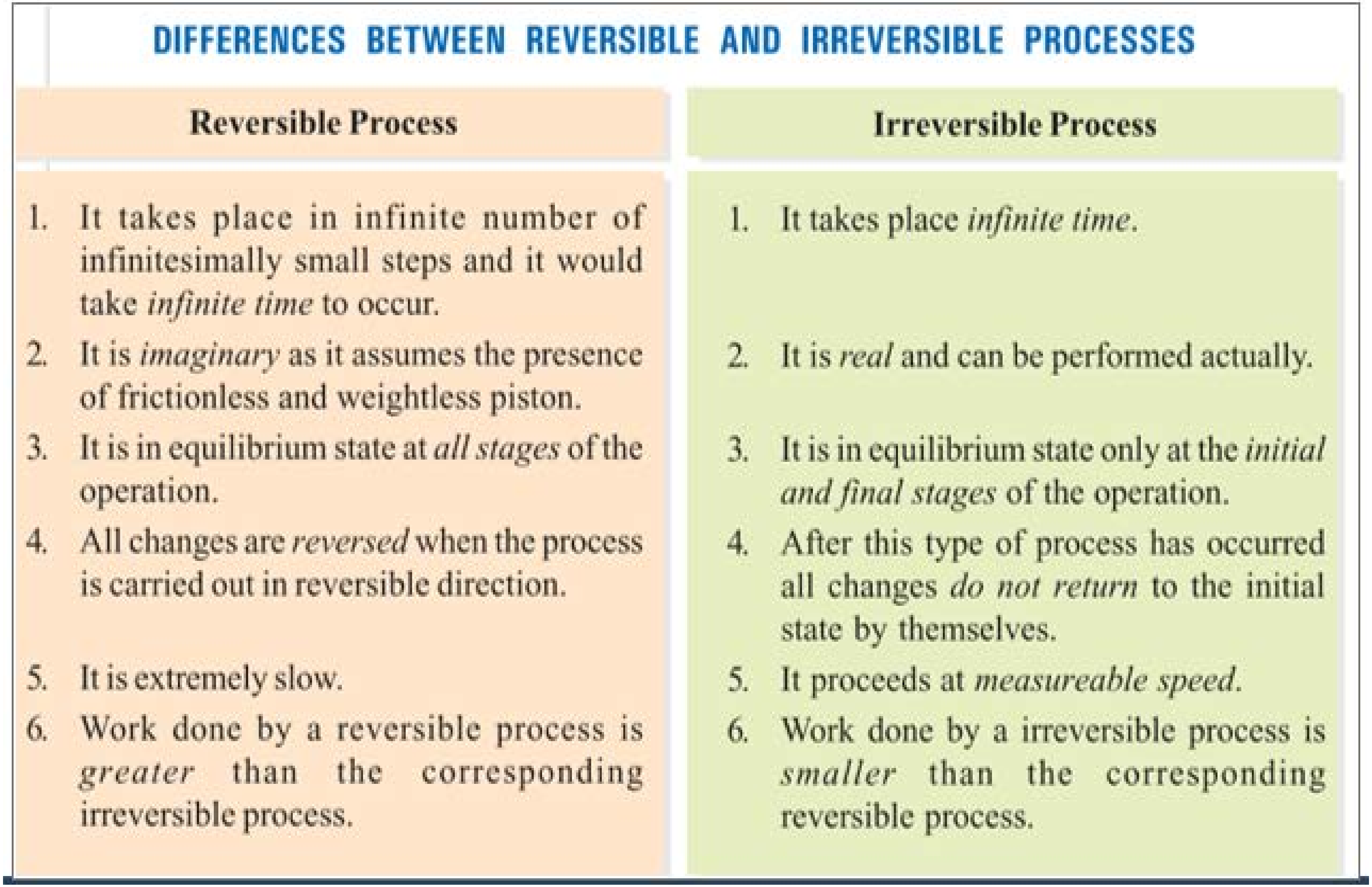
Fundamental Concepts

Properties changes

- in reversible (idealize equilibrium) and irreversible (spontaneous) processes with time



Fundamental Concepts



DIFFERENCES BETWEEN REVERSIBLE AND IRREVERSIBLE PROCESSES

Reversible Process	Irreversible Process
1. It takes place in infinite number of infinitesimally small steps and it would take *infinite time* to occur.	1. It takes place *infinite time*.
2. It is *imaginary* as it assumes the presence of frictionless and weightless piston.	2. It is *real* and can be performed actually.
3. It is in equilibrium state at *all stages* of the operation.	3. It is in equilibrium state only at the *initial and final stages* of the operation.
4. All changes are *reversed* when the process is carried out in reversible direction.	4. After this type of process has occurred all changes *do not return* to the initial state by themselves.
5. It is extremely slow.	5. It proceeds at *measureable speed*.
6. Work done by a reversible process is *greater* than the corresponding irreversible process.	6. Work done by a irreversible process is *smaller* than the corresponding reversible process.

Spontaneity and Internal Energy (U)

Criteria in terms of U

- 1^{st} law of thermodynamics

$$dU = dq - pdV$$

$$\Longrightarrow dq = dU + pdV$$

- 2^{nd} law of thermodynamics

$$\frac{dq}{T} \leq dS$$

$$\Longrightarrow dq \leq TdS$$

- Combing 1^{st} and 2^{nd} laws of thermodynamics

$$dU + pdV \leq TdS$$

$$dU \leq -pdV + TdS$$

- At constant V and S, $dV = 0$ and $dS = 0$

$$dU_{V,S} \leq 0$$

Interpretation of the criteria:

a) The decrease (negative change) in U at constant V and S refers to the irreversible/spontaneous processes

b) No change ($dU = 0$) in U at constant V and S indicates reversible process or the system at equilibrium.

Limitations:

a) Calculation of dU at constant V and S is quite difficult because the maintain of constant S is cumbersome.

b) The negative change in U ($dU < 0$) representing exothermic processes may either be spontaneous or non-spontaneous.

  - Melting of ice is spontaneous but $dU > 0$.

Spontaneity and Enthalpy (H)

Criteria in terms of H

- 1st law of thermodynamics

$$dU = dq - pdV$$
$$dq = dU + pdV + Vdp - Vdp$$
$$dq = dU + d(pV) - Vdp$$
$$dq = d(U + pV) - Vdp$$
$$dq = dH - Vdp$$

- 2nd law of thermodynamics

$$\frac{dq}{T} \le dS \Longrightarrow dq \le TdS$$

- Combing 1st and 2nd laws of thermodynamics

$$dH - Vdp \le TdS$$
$$dH \le Vdp + TdS$$

- At constant p and S, $dp = 0$ and $dS = 0$

$$dH_{p,S} \le 0$$

Interpretation of the criteria:

a) The decrease (negative change) in H at constant p and S refers to the irreversible/spontaneous processes

b) No change ($dH = 0$) in H at constant p and S indicates reversible process or the system at equilibrium.

Limitations:

a) Calculation of dH at constant p and S is quite difficult because the maintain of constant S is cumbersome.

b) The negative change in H ($dH < 0$) representing exothermic processes may either be spontaneous or non-spontaneous.

   - Melting of ice is spontaneous but $dH > 0$.

Spontaneity and Entropy (S)

Criteria in terms of S

- 1^{st} law of thermodynamics

$$dU = dq - pdV$$
$$\Longrightarrow dq = dU + pdV \qquad (1)$$
$$dq = dU + pdV + Vdp - Vdp$$
$$dq = dU + d(pV) - Vdp$$
$$dq = d(U + pV) - Vdp$$
$$dq = dH - Vdp \qquad (2)$$

- 2^{nd} law of thermodynamics

$$dS \geq dq/T \qquad (3)$$

- From eq. (1) & (3)

$$dS \geq (dU + pdV)/T$$

- At constant U & V, $dU = 0$, $dV = 0$

$$dS_{U,V} \geq 0$$

- From eq. (2) & (3)

$$dS \geq (dH - Vdp)/T$$

- At constant H & p, $dH = 0$, $dp = 0$

$$dS_{H,p} \geq 0$$

Interpretation of the criteria:

a) The increase (positive change) in S at constant U & V or at constant H & p refers to the irreversible/spontaneous processes

b) No change ($dS = 0$) in S under these conditions indicates reversible process or the system at equilibrium.

Limitations:

a) Predicting spontaneity based on entropy change ($dS \geq 0$) requires calculating entropy changes for both the system and its surroundings.

b) Calculating the entropy change of the surroundings can be challenging, as the changes are often very small and difficult to determine accurately.

Need new thermodynamic functions

- The use of dU, dH or dS for the criteria of spontaneity or equilibrium encounters the following challenges:
  - (a) The use of $(dU)_{S,V}$ or $(dH)_{S,P}$ requires the condition of constant entropy which is not easy to maintain.
  - (b) The use of $dS_{univ} > 0$ requires the calculation of both dS_{sys} and dS_{surr}. One feels bother directly about the surroundings while concentrating on investigation of systems.
- Hence we need new thermodynamic functions of system that meet the following requirements:
  - Must be able to predict the processes of direction
  - Automatically incorporate dH or dU and dS of system
  - Account dS of both system and surrounding if required
- Two new thermodynamic functions are Gibbs energy or Gibbs free energy denoted by G and Helmholtz energy or work function denoted by F or A.

Definition of Helmholtz free energy

Consider material equilibrium at constant T and V

$$dU \le TdS + dw$$

$$dU \le TdS + \underbrace{SdT}_{} - SdT + dw$$

$$dU \le d(TS) - SdT + dw$$

$$d(U - TS) \le - SdT + dw$$

dw = -P dV for P-V work only

$$d(U - TS) \le \cancel{- SdT} - \cancel{PdV}$$

at constant T and V, dT=0, dV=0

$$d(U - TS) \le 0$$

Equality sign holds at material equilibrium

$$\boxed{A \equiv U - TS}$$

Significance of Helmholtz free energy

Using Clausius inequality $dS \geq \frac{dq}{T}$ in the form $TdS \geq dq$ in first law, $dw = dU - dq$, gives $dw \geq dU - TdS$

$$\Longrightarrow w \geq \Delta U - T\Delta S \qquad (1)$$

In eq 1 *w* is interpreted as maximum energy that can be obtained from the system as work which is done reversibly. Therefore, *w* for reversible processes is given by

$$w_{max} = \Delta U - T\Delta S \qquad (2)$$

From the definition of Helmholtz free energy

$$A = U - TS \Longrightarrow \Delta A = \Delta U - T\Delta S - S\Delta T$$

For isothermal changes, $\Delta \mathrm{T} = 0$

$$\Delta A = \Delta U - T\Delta S \qquad (3)$$

From eq 2 and 3 we obtain, $w_{max} = \Delta A$

The change in the Helmholtz energy is equal to the maximum work.

Definition of Gibbs free energy

Consider material equilibrium for constant T & P

$dU \leq T\,dS + dw$ **with** $dw = -PdV$

$dU \leq T\,dS + S\,dT - S\,dT - P\,dV - V\,dP + V\,dP$

$dU \leq d(TS) - SdT - d(PV) + VdP$

$d(\underline{U + PV} - TS) \leq -SdT + VdP$

$d(H - TS) \leq - SdT + VdP$

At constant T & P, dT = 0, dP = 0

$d(H - TS) \leq 0$

$G \equiv H - TS \equiv U + PV - TS$

Significance of Gibbs free energy

From the definition of G

$G = U + PV - TS$

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

From 2nd law, $TdS = dq$

From first law, $dU = dq + dw = TdS + dw$

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

At constant T & P, $dT = 0, dP = 0$

$dG = dw + PdV \Rightarrow \Delta G = w + P\Delta V$

The mechanical work involving P-V work is defined as

$w_{mecha} = -P\Delta V$

w is splitted as $w = w_{non-mecha} + w_{mecha}$

Significance of Helmholtz free energy

$$\Delta G = w_{non-mecha} + w_{mecha} - w_{mecha}$$
$$\Delta G = w_{non-mecha}$$

The mechanical work maintains the system’s volume only. It does not contribute to any thermodynamic processes.

On the other hands, non-mechanical work contributes to the thermodynamic processes. So, it is called useful work or net work.

It turns out that G carries a greater significance that being simply a signpost of spontaneous change:

$$\Delta G = w_{net}$$

The change in the Helmholtz energy is equal to the net work

Relation between ΔG_{sys} and ΔS_{univ}

At Constant T and P

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} \qquad (1)$$

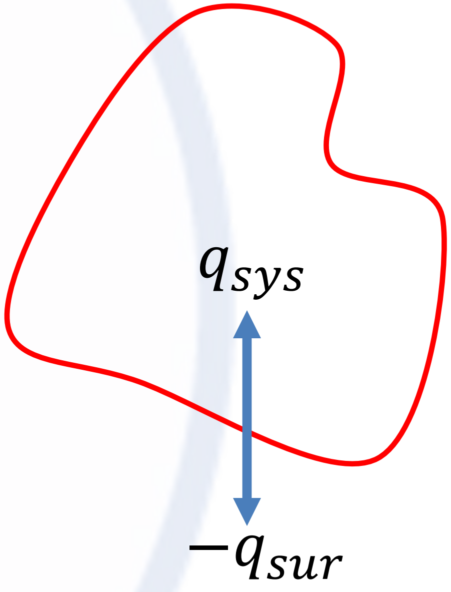
Heat exchange between system and surrounding is the same in magnitude but opposite in sign

$$q_{sys} = -q_{sur}$$

At constant P, system's enthalpy change is given by the heat exchange between system and its surroundings

$$\Delta H_{sys} = q_{sys}$$

$$\Rightarrow \Delta H_{sys} = T(q_{sys}/\mathrm{T})$$
$$\Rightarrow \Delta H_{sys} = -T(q_{sur}/\mathrm{T})$$
$$\Rightarrow \Delta H_{sys} = -T\Delta S_{sur} \qquad (2)$$



From eqs. 1 and 2

$$\Delta G_{sys} = -T\Delta S_{sur} - T\Delta S_{sys}$$

$$\Rightarrow \Delta G_{sys} = -T(\Delta S_{sur} + \Delta S_{sys})$$

Using $\Delta S_{univ} = \Delta S_{sur} + \Delta S_{sys}$

$$\Rightarrow \Delta G_{sys} = -T\Delta S_{univ}$$
$$\Rightarrow -\Delta G_{sys} = T\Delta S_{univ}$$

The decrease in the free energy of the system is equal to increase in the entropy of the universe multiplied by the kelvin temperature.

Spontaneity and Helmholtz Energies

From the definition of Helmholtz energy

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

$$TdS = -dA + dU - SdT$$

From Cassius inequality and 1st law of thermodynamics

$$dS \geq \frac{dq}{T} \Longrightarrow TdS \geq dq \Longrightarrow TdS \geq dU + pdV$$

Combining

$$-dA + dU - SdT \geq dU + pdV$$

$$-dA \geq SdT + pdV$$

$$dA \leq -pdV - SdT$$

At constant T & V, $dT = 0$, $dV = 0$

$$dA_{T,V} \leq 0$$

Spontaneity and Gibbs Energies

From the definition of Gibbs energy

$$G = H - TS$$

$$G = U + pV - TS$$

$$dG = dU + pdV + Vdp - TdS - SdT$$

$$TdS = -dG + dU + pdV + Vdp - SdT$$

From Cassius inequality and 1st law of thermodynamics

$$dS \geq \frac{dq}{T} \Longrightarrow TdS \geq dq \Longrightarrow TdS \geq dU + pdV$$

Combining

$$-dG + dU + pdV + Vdp - SdT \geq dU + pdV$$

$$dG \leq -SdT + Vdp$$

At constant T & p, $dT = 0$, $dp = 0$

$$dG_{T,p} \leq 0$$

Relation among ΔG , ΔH and ΔS

- From the definition of G,

$$A = U - TS$$

- For large or measurable change

$$\Delta A = \Delta U - T\Delta S - S\Delta T$$

- For iso thermal processes, $\Delta T = 0$

$$\Delta A = \Delta U - T\Delta S$$

Gibbs Free energy equation
or simply Gibbs equation

- From the definition of G,

$$G = H - TS$$

- For large or measurable change

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

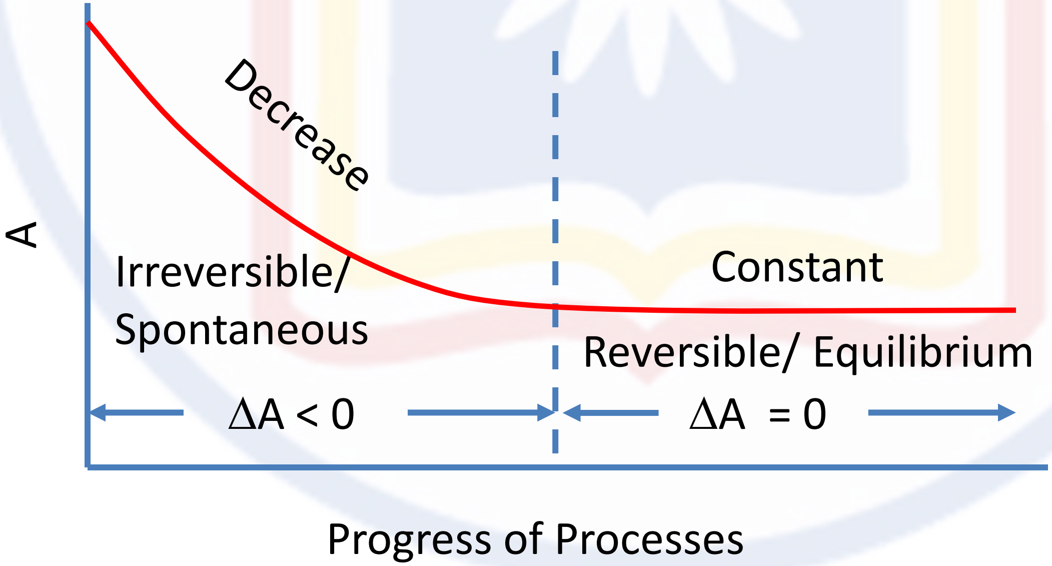
- For iso thermal processes, $\Delta T = 0$

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

Gibbs Free energy equation
or simply Gibbs equation

Helmholtz energy & Equilibrium

- For a closed system (T & V constant), the state function *U-TS, continually decrease during the spontaneous, irreversible process of chemical reaction and matter transport until material equilibrium is reached*
- *d(U-TS)=0   at equilibrium*
- *dA = 0* at constant T & V for closed system



GIBSS & HELMHOLTZ ENERGIES

A spontaneous process at constant T and V is accompanied by a decrease in the **Helmholtz energy, *A* or *F*.**

A spontaneous process at constant T and P is accompanied by a decrease in the **Gibbs energy, *G***.

dA = 0 *at equilibrium, const. T, V*

dG = 0 *at equilibrium, const. T, P*

- **ADVANTAGES OF USING ΔA AND ΔG OVER ΔS**

1. Use of ΔS to predict the nature of a process requires the knowledge of both ΔS_{sys} and ΔS_{sur}.
   - But ΔG or ΔA of the system alone is sufficient to predict the direction of a process.
2. While using ΔS it is required that energy and volume are constant $\Delta S_{U,V} > 0$.
   - But it is not very convenient to maintain a constant energy condition in the laboratory.
   - On the other hand, while using ΔA or ΔG only the state variables (T, V, or T, P) are to be kept constant, which are easy to maintain in the laboratory.

Therefore, the use of ΔA or ΔG is preferred over ΔS as a driving force to predict the direction of a process

- **Advantages of using ΔG over ΔA**

  - When ΔG is used to predict the direction of a process it is required to maintain constant T and P as $\Delta G_{T,P} < 0$ for a spontaneous process
  - On the other hand, if ΔA is used to decide the direction of a process the T and V are to be kept constant as $\Delta A_{T,V} < 0$ for spontaneous process.
  - Since in the chemistry laboratory usually the experiments are performed at constant T and P, therefore, the use of ΔG as driving force is preferred over the use of ΔA which requires the condition of constant T and V.

Thermodynamic Relations for a System

6 Basic Equations:

- $dU = TdS - PdV$ closed syst, rev, proc, P-V work only
- $H = U + PV$
- $A = U - TS$
- $G = H - TS$
- $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ *closed syst., in equilib., P-V work only*
- $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ *closed syst., in equilib., P-V work only*

The rates of change of *U*, *H*, and *S* with respect to *T* can be determined from the heat capacities C_P and C_V.

Heat Capacities (C_P & C_V) are key properties

The Gibbs Equations

$$\left.\begin{aligned} dU &= TdS - PdV \\ dH &= TdS + VdP \\ dA &= -SdT - PdV \\ dG &= -SdT + VdP \end{aligned}\right\} \text{\textit{closed syst., rev. proc., P-V work only}}$$

How to derive *dH, dA and dG*?

The Gibbs Equations

$$dH = ?$$

$$H \equiv U + PV$$

$$dH = d(U + PV)$$

$$= dU + d(PV)$$

$$= \underline{dU} + PdV + VdP$$

$dU = TdS - PdV$

$$= (TdS - \cancel{PdV}) + \cancel{PdV} + VdP$$

$$\mathbf{dH = TdS + VdP}$$

$dA = ?$

$$A \equiv U - TS$$

$$dA = d(U - TS)$$

$$= dU - d(TS)$$

$$= \underline{dU} - TdS - SdT$$

$$= (\cancel{TdS} - PdV) - \cancel{TdS} - SdT$$

$$\boxed{dA = -SdT - PdV}$$

$dU = TdS - PdV$

$dG = ?$

$$G \equiv H - TS$$

$$dG = d(H - TS)$$

$$= dH - d(TS)$$

$$= \underline{dH} - TdS - SdT$$

$$= (\cancel{TdS} + VdP) - \cancel{TdS} - SdT$$

$$\boxed{dG = -SdT + VdP}$$

$dH = TdS + VdP$

The Gibbs equation $dU = T\,dS - P\,dV$ implies that U is being considered a function of the variables S and V. From U= U (S,V) we have

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \qquad (dU = TdS - PdV)$$

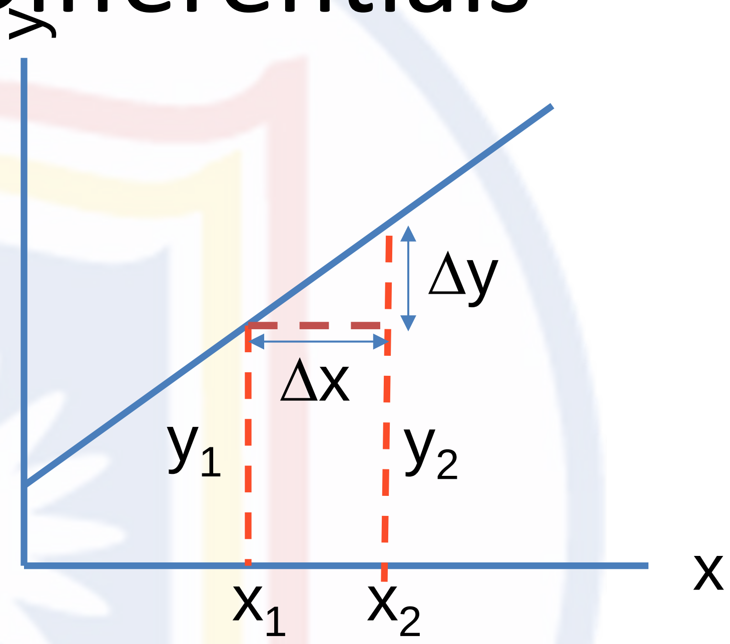
$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \left(\frac{\partial G}{\partial P}\right)_T = V \qquad (dG = -SdT + VdP)$$

The Power of thermodynamics:

Difficultly measured properties to be expressed in terms of *easily measured* properties.

Derivatives & Differentials



Derivative: The rate of change of dependent variable, y wrt independent variable, x

$$f'(x) = \frac{\Delta y}{\Delta x}$$

For infinitesimal changes

$$f'(x) = \frac{\mathrm{d}y}{\mathrm{d}x}$$

Differentials: The change of variables (x,y). The Δx, Δy are differentials of x and y, respectively.

Relationship:

$\Delta y = f'(x)\Delta \mathrm{x}$ for large changes (differential)

$dy = f'(x)dx$ for infinitesimal changes (differential)

Exact differentials

Let z = f(x,y)

$$\left(\frac{\partial z}{\partial x}\right)_y = M$$

$$\left(\frac{\partial z}{\partial y}\right)_x = N$$

$dz_x = Mdx$ and $dz_y = Ndy$

$$dz = dz_x + dz_y = Mdx + Ndy$$

dz is said to be exact differential if

$$\frac{dM}{dy} = \frac{dN}{dx} \qquad \frac{d}{dy}\left(\frac{\partial z}{\partial x}\right) = \frac{d}{dx}(\frac{\partial z}{\partial y})$$

$$\frac{d^2z}{dydx} = \frac{d^2z}{dxdy}$$

The Euler Reciprocity Relations

If Z＝f(x，y)，and Z has continuous second partial derivatives, then

$$dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy$$

$$dZ = M dx + N dy \quad M = \left(\frac{\partial Z}{\partial x}\right)_y \quad N = \left(\frac{\partial Z}{\partial y}\right)_x$$

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

That is $$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

State Function

Show that dq_{rev}/T is a state function but dq_{rev} is not.

From 1st law of thermodynamics

$$dq_{rev} = dU + pdV$$

Since $U = U(T,V)$, then

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

$$dq_{rev} = C_V dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{=0} dV + \frac{nRT}{V} dV$$

$$dq_{rev} = C_V dT + (nRT/V)dV$$

$$dq_{rev} = MdT + NdV$$

$$M = C_V, N = nRT/V$$

$$\left(\frac{\partial M}{\partial V}\right)_T = \left(\frac{\partial C_V}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial N}{\partial T}\right)_V = -\frac{nR}{V}$$

$$\left(\frac{\partial M}{\partial V}\right)_T \neq \left(\frac{\partial N}{\partial T}\right)_V$$

$$dq_{rev}/T = (C_V/T)dT + (nR/V)dV$$

$$dq_{rev} = MdT + NdV$$

$$M = C_V/T, N = nR/V$$

$$\left(\frac{\partial M}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial N}{\partial T}\right)_V = 0$$

$$\left(\frac{\partial M}{\partial V}\right)_T = \left(\frac{\partial N}{\partial T}\right)_V$$

The Maxwell Relations

(Application of Euler relation to Gibbs equations)

dU = TdS - PdV

The Gibbs equation (4.33) for *dU* is

$$dU = TdS - PdV$$

$dS = 0$ $\qquad$ $dV = 0$

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

Applying Euler Reciprocity,

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)$$

$$\frac{\partial}{\partial V}(T)_S = \frac{\partial}{\partial S}(-P)_V \quad \Rightarrow \quad -\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S$$

These are the Maxwell Relations

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

The first two are little used.

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

The last two are extremely valuable.

The equations relate the isothermal pressure and volume variations of entropy to *measurable* properties.

Dependence of State Functions on T, P, and V

- We now find the dependence of U, H, S and G on the variables of the system.
- The most common independent variables are T and P.
- We can relate the temperature and pressure variations of H, S, and G to the measurable Cp, α, and κ

Volume dependence of *U*

The Gibbs equation gives $dU = TdS - PdV$

Divide both sides by dV keeping T constant

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

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

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

From Euler's chain rule, $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P = -1$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P / \left(\frac{\partial V}{\partial P}\right)_T = \frac{-\alpha V}{-\kappa V} = \frac{\alpha}{\kappa}$$

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

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Pressure dependence of *H*

From Gibbs equations, $dH = TdS + VdP$

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

From Maxwell Relationship

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

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V = -TV\alpha + V$$

$$\boxed{\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P}$$

Temperature dependence of S

From Gibbs Equations,

$dU = TdS - PdV$

Divide both sides by *dT* keeping *V* constant

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

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

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

From Gibbs Equations,

$dH = TdS + VdP$

Divide both sides by *dT* keeping *P* constant

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

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

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

Pressure dependence of *S*

From Maxwell Relations

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

Temperature & Pressure dependence of *G*

The Gibbs equation for *dG* is

$$\begin{tikzcd} & \mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P \arrow[dl, "\mathrm{d}T=0"] \arrow[dr, "\mathrm{d}P=0"] & \\ \left(\frac{\partial G}{\partial P}\right)_T = V & & \left(\frac{\partial G}{\partial T}\right)_P = -S \end{tikzcd}$$

Joule-Thomson Coefficient

From definition, $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$ which links variables *T, P, H*

Applying Euler's chain rule for these variables

$$\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial P}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_P = -1$$

$$\mu_{JT} = -\left(\frac{\partial H}{\partial P}\right)_T \Big/ \left(\frac{\partial H}{\partial T}\right)_P$$

From pressure dependence of H

$$\mu_{JT} = -\left(\frac{\partial H}{\partial P}\right)_T / C_P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -TV\alpha + V$$

$$\mu_{JT} = -(-TV\alpha + V)/C_P$$

$$\mu_{JT} = (T\alpha - 1)(V/C_P)$$

Heat-Capacity Difference

(easily measured quantities)

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$PV = RT$$

$$P\left(\frac{\partial V}{\partial T}\right)_P = R$$

From volume dependence of U

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

$$C_P - C_V = \left(\frac{\alpha T}{\kappa}\right)\left(\frac{\partial V}{\partial T}\right)_P$$

$$\alpha \equiv V^{-1}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial V}{\partial T}\right)_P \equiv \alpha V$$

$$C_P - C_V = \frac{TV\alpha^2}{\kappa}$$

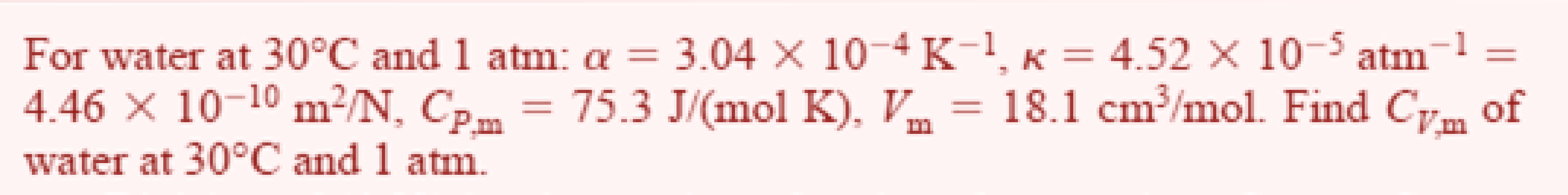
Heat-Capacity Difference

$$C_P - C_V = \frac{TV\alpha^2}{\kappa}$$

1. As $T \to 0$, $C_P \to C_V$
2. $C_P \geq C_V$ (since $\kappa > 0$)
3. $C_P = C_V$ (if $\alpha = 0$)

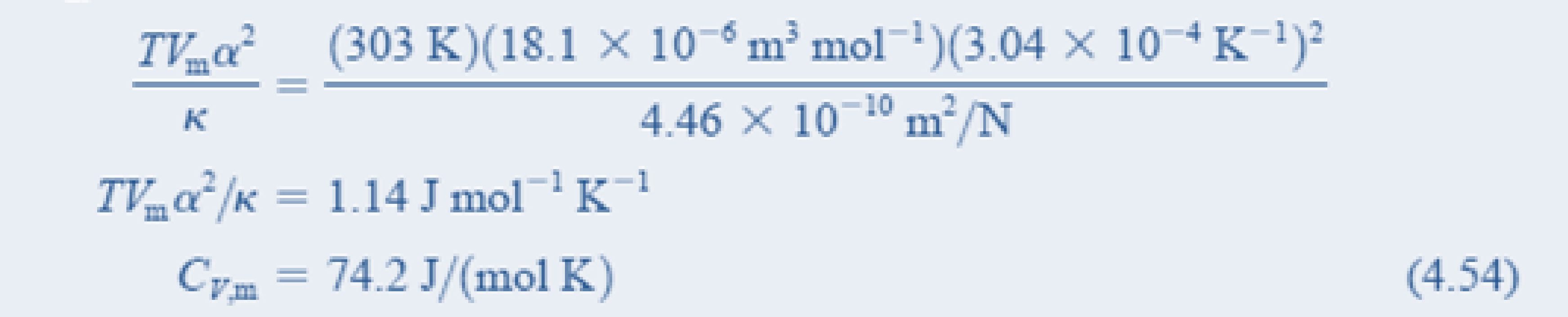
EXAMPLE 1

$C_P - C_V$



For water at 30°C and 1 atm: $\alpha = 3.04 \times 10^{-4}\ \mathrm{K}^{-1}$, $\kappa = 4.52 \times 10^{-5}\ \mathrm{atm}^{-1} = 4.46 \times 10^{-10}\ \mathrm{m^2/N}$, $C_{P,\mathrm{m}} = 75.3\ \mathrm{J/(mol\ K)}$, $V_\mathrm{m} = 18.1\ \mathrm{cm^3/mol}$. Find $C_{V,\mathrm{m}}$ of water at 30°C and 1 atm.

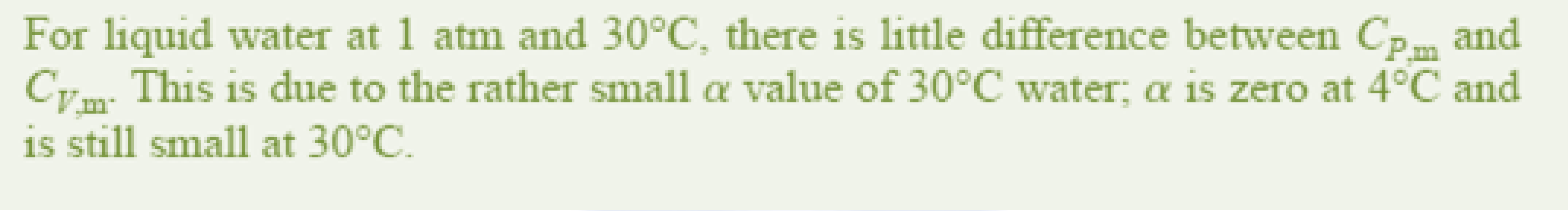
$$C_P - C_V = \frac{TV\alpha^2}{\kappa} \xrightarrow{\div n} C_{P,m} - C_{V,m} = \frac{TV_m\alpha^2}{\kappa}$$



$$\frac{TV_\mathrm{m}\alpha^2}{\kappa} = \frac{(303\ \mathrm{K})(18.1 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}})(3.04 \times 10^{-4}\ \mathrm{K^{-1}})^2}{4.46 \times 10^{-10}\ \mathrm{m^2/N}}$$

$$TV_\mathrm{m}\alpha^2/\kappa = 1.14\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

$$C_{V,\mathrm{m}} = 74.2\ \mathrm{J/(mol\ K)} \tag{4.54}$$



For liquid water at 1 atm and 30°C, there is little difference between $C_{P,\mathrm{m}}$ and $C_{V,\mathrm{m}}$. This is due to the rather small α value of 30°C water; α is zero at 4°C and is still small at 30°C.

$\left(\frac{\partial U}{\partial V}\right)_T$ Internal Pressure

Ideal gases $\left(\frac{\partial U}{\partial V}\right)_T = 0$

Solids, Liquids, & Non-ideal Gases

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

Solids	300 J/cm^3 (25 $^{\text{o}}$C, 1 atm)
Liquids	300 J/cm^3 (25 $^{\text{o}}$C, 1 atm)

↓

Strong intermolecular forces in solids and liquids.

❖Calculation of Changes in State Function

1. Calculation of ΔS

Suppose a closed system of constant composition goes from state (P_1,T_1) to state (P_2,T_2), the system's entropy is a function of T and P

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

$$dS = \frac{C_P}{T} dT - \alpha V dP$$

Integration gives:

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{C_P}{T} dT - \int_1^2 \alpha V dP$$

Since S is a state function, ΔS is independent of the path used to connect states 1 and 2. A convenient path (Figure 4.3) is first to hold P constant at P_1 and change T from T_1 to T_2. Then T is held constant at T_2, and P is changed from P1 to P2.

For step (a), dP=0 and gives

$$\Delta S_a = \int_{T_1}^{T_2} \frac{C_P}{T} dT \qquad const \quad P = P_1$$

For step (b), dT=0 and gives

$$\Delta S_b = -\int_{P_1}^{P_2} \alpha V dP \qquad const \quad T = T_2$$

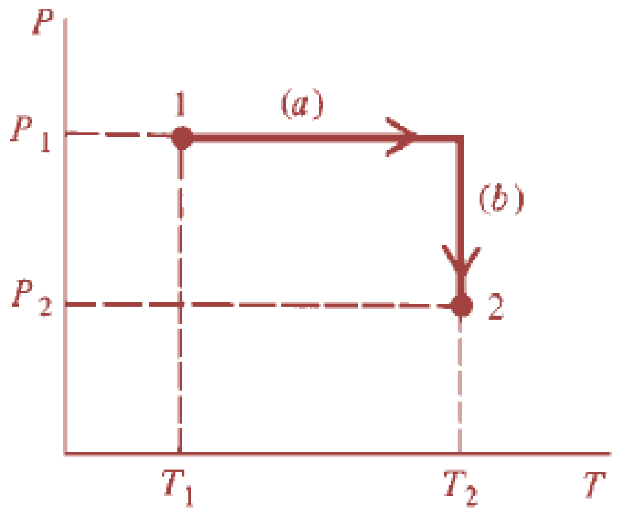
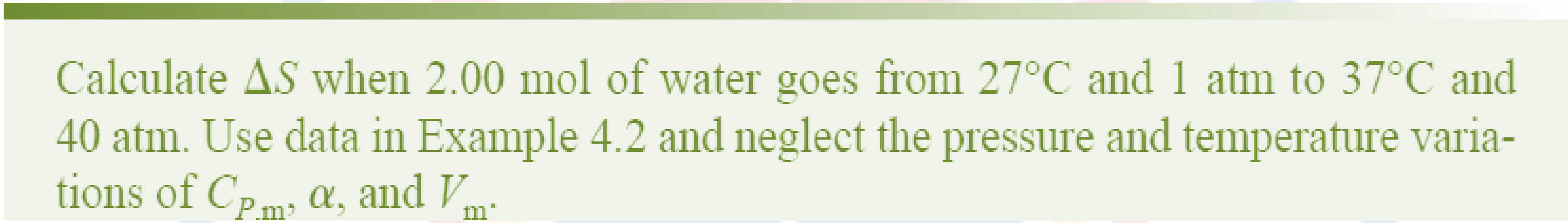


Figure 4.3

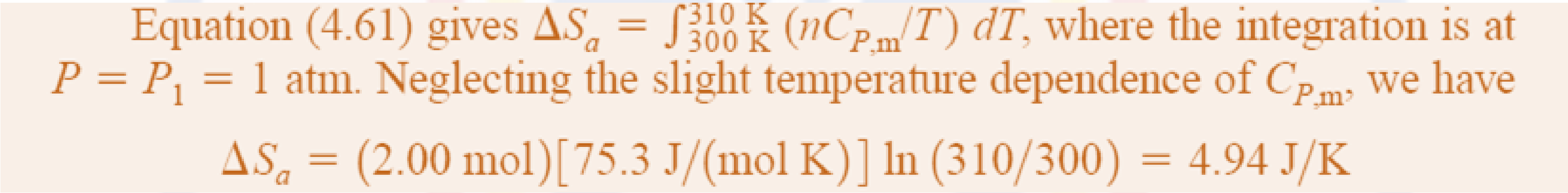
Path for calculating ΔS or ΔH.

EXAMPLE 2

ΔS when both T and P change

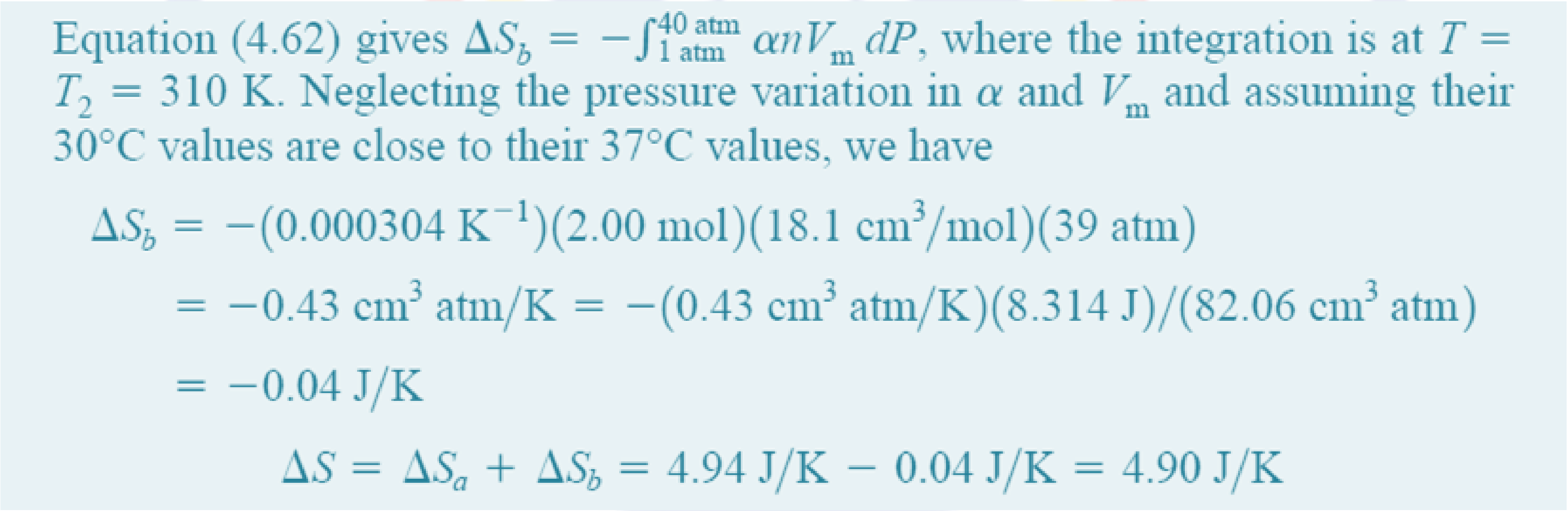


Calculate ΔS when 2.00 mol of water goes from 27°C and 1 atm to 37°C and 40 atm. Use data in Example 4.2 and neglect the pressure and temperature variations of $C_{P,\mathrm{m}}$, α, and V_{m}.



Equation (4.61) gives $\Delta S_a = \int_{300\text{ K}}^{310\text{ K}} (nC_{P,\mathrm{m}}/T)\, dT$, where the integration is at $P = P_1 = 1$ atm. Neglecting the slight temperature dependence of $C_{P,\mathrm{m}}$, we have

$$\Delta S_a = (2.00\text{ mol})[75.3\text{ J/(mol K)}] \ln (310/300) = 4.94\text{ J/K}$$



Equation (4.62) gives $\Delta S_b = -\int_{1\text{ atm}}^{40\text{ atm}} \alpha n V_{\mathrm{m}}\, dP$, where the integration is at $T = T_2 = 310$ K. Neglecting the pressure variation in α and V_{m} and assuming their 30°C values are close to their 37°C values, we have

$$\begin{aligned}\Delta S_b &= -(0.000304\text{ K}^{-1})(2.00\text{ mol})(18.1\text{ cm}^3/\text{mol})(39\text{ atm})\\ &= -0.43\text{ cm}^3\text{ atm/K} = -(0.43\text{ cm}^3\text{ atm/K})(8.314\text{ J})/(82.06\text{ cm}^3\text{ atm})\\ &= -0.04\text{ J/K}\end{aligned}$$

$$\Delta S = \Delta S_a + \Delta S_b = 4.94\text{ J/K} - 0.04\text{ J/K} = 4.90\text{ J/K}$$

2. Calculation of ΔH

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

$$= C_P dT + (-TV\alpha + V)dP$$

$$\Delta H = \int_1^2 C_P \; dT + \int_1^2 (V - TV\alpha) \; dP$$

ΔU can be easily found from ΔH using :

$$\Delta U = \Delta H - \Delta\,(PV)$$

Alternatively we can write down the equation for ΔU similar to:

3. Calculation of ΔG

For isothermal process:

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

Alternatively, ΔG for an isothermal process that does not involve an irreversible composition change can be found as:

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$dG = VdP$$

$$\Delta G = \int_{P1}^{P2} VdP$$

A special case:

$$\Delta G = 0 \quad rev \quad process \quad at \quad const \quad T \quad and \quad P$$

[Since $\Delta H = q, \quad \Delta S = q / T$]