

Physical Chemistry

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(Sixth edition)

Bilingual

Program

Part 1: Equilibrium

5. The Second Law: the machinery

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Program



5. The Second Law: the machinery

In this chapter:

First: to find relations between properties that might not be thought to be related; to derive expressions for the variation of the G with T and p .

Second: to introduce the **chemical potential**, a property that will be at the center of discussions in the remaining chapters of this part of the text; to derive expression of **fugacity**.

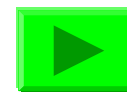
The '**chemical potential**', the quantity on which almost all the most important applications of thermodynamics to chemistry are based.



5. The Second Law: the machinery

Combing the First and Second Laws

5.1 Properties of the internal energy



5.2 Properties of the Gibbs energy

5.3 The chemical potential of a pure substance

Real gases:the fugacity

5.4 The definition of fugacity

5.5 Standard states of real gases

5.6 The relation between fugacity and pressure



The fundamental equations

Five state functions in the First and Second Laws:

The internal energy: U

The entropy: S

The enthalpy: H

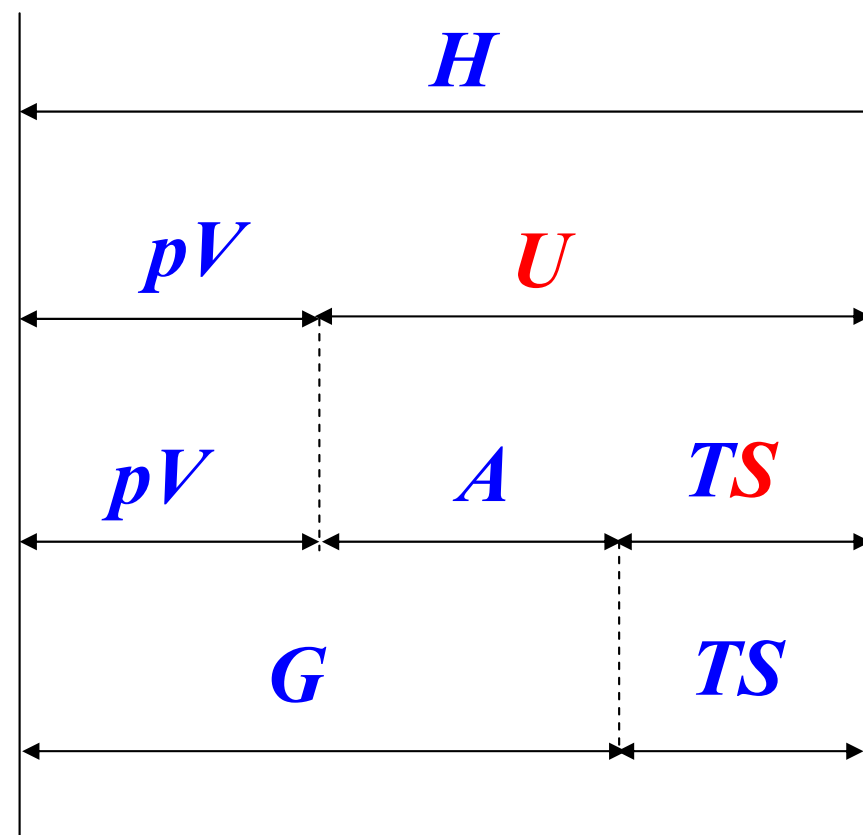
The Helmholtz energy: A

The Gibbs energy: G

$$H = U + pV$$

$$A = U - TS$$

$$G = H - TS = U + pV - TS = A + pV$$





The fundamental equations

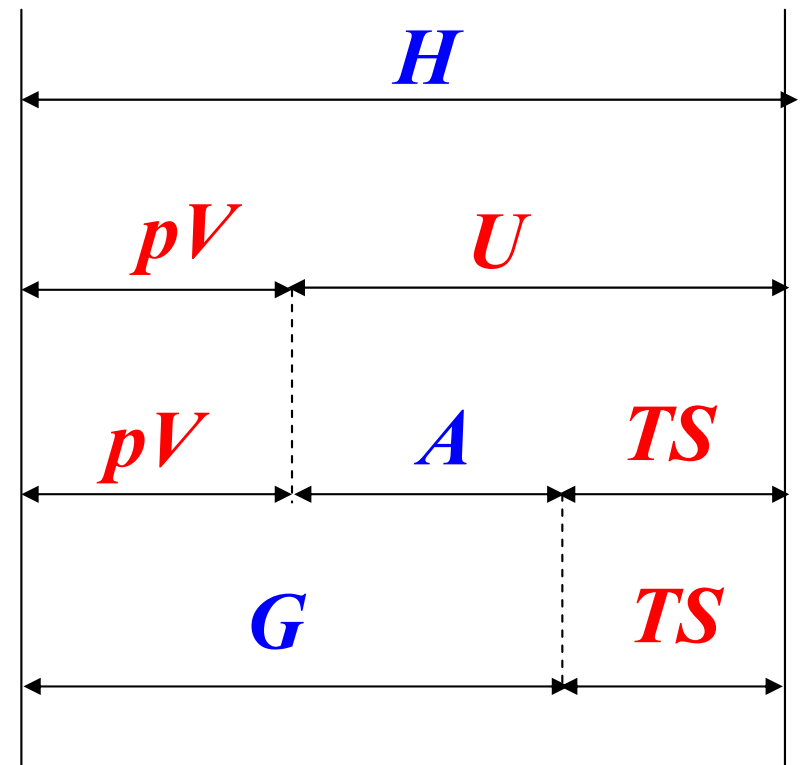
The First Law: $dU = dq + dw$

For a reversible change in a closed system of constant composition, and in the absence of any non-expansion work:

$$dw = -pdV \quad \text{and} \quad dq = TdS$$

$$dU = TdS - pdV$$

dU is an exact differential, its value is independent of path.





The fundamental equations

$$H=U+pV, \quad A=U-TS, \quad G=U+pV-TS$$

$$dH = dU + pdV + Vdp$$

$$= (\cancel{TdS} - \cancel{pdV}) + \cancel{pdV} + Vdp$$

$$= TdS + Vdp$$

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

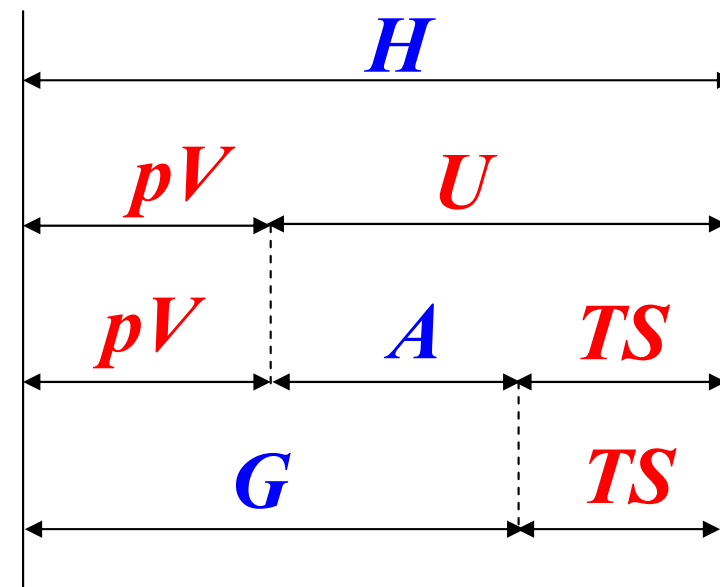
$$= (\cancel{TdS} - \cancel{pdV}) + \cancel{pdV} + Vdp - \cancel{TdS} - SdT$$

$$= Vdp - SdT$$

$$dA = dU - TdS - SdT$$

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

$$= -pdV - SdT$$





The fundamental equations

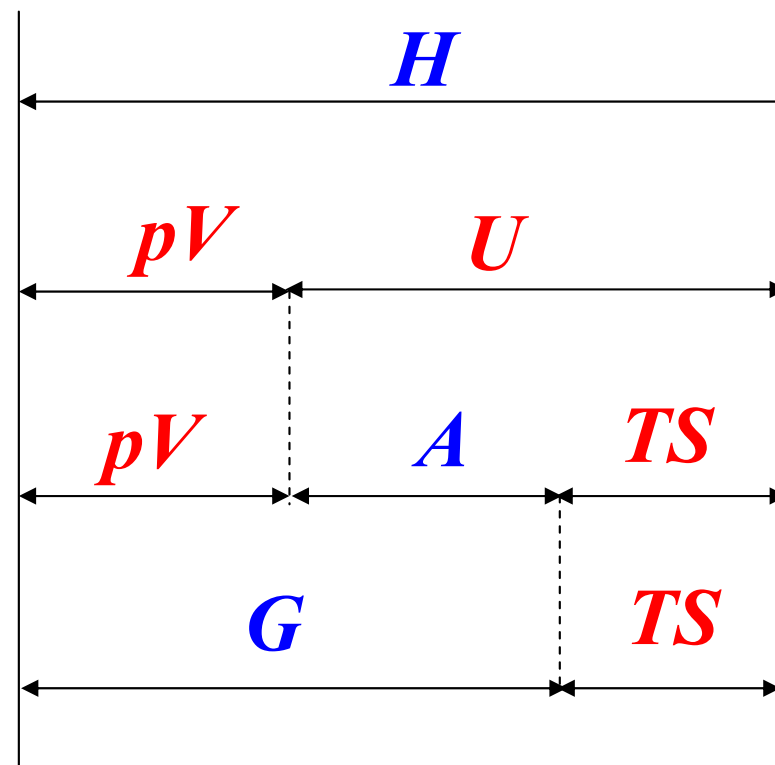
$$dU = TdS - pdV$$

$$dH = TdS + Vdp$$

$$dG = Vdp - SdT$$

$$dA = -pdV - SdT$$

The fundamental equations





5.1 Properties of the internal energy

1). The Maxwell relations

$$z = f(x, y) \quad \mathbf{dz} = \left(\frac{\partial z}{\partial x} \right)_y \mathbf{dx} + \left(\frac{\partial z}{\partial y} \right)_x \mathbf{dy}$$
$$= \mathbf{gdx} + \mathbf{hdy}$$

$$\text{where } \mathbf{g} = \left(\frac{\partial z}{\partial x} \right)_y, \quad \mathbf{h} = \left(\frac{\partial z}{\partial y} \right)_x$$



5.1 Properties of the internal energy

1). The Maxwell relations

The first derivative of g with respect to y , and h to x

$$\left. \begin{aligned} \left(\frac{\partial g}{\partial y} \right)_x &= \frac{\partial^2 z}{\partial x \partial y} \\ \left(\frac{\partial h}{\partial x} \right)_y &= \frac{\partial^2 z}{\partial y \partial x} \end{aligned} \right\} \left(\frac{\partial g}{\partial y} \right)_x = \left(\frac{\partial h}{\partial x} \right)_y$$

$$dz = gdx + hdy$$



5.1 Properties of the internal energy

1). The Maxwell relations

$$\left. \begin{aligned} dz &= gdx + hdy \\ dU &= TdS - pdV \end{aligned} \right\} dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV$$

$$g = \left(\frac{\partial U}{\partial S} \right)_V = T, \quad h = \left(\frac{\partial U}{\partial V} \right)_S = -p$$

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V \qquad \left(\frac{\partial g}{\partial y} \right)_x = \left(\frac{\partial h}{\partial x} \right)_y$$



5.1 Properties of the internal energy

1). The Maxwell relations

$$dU = TdS - pdV \quad \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V$$

$$dH = TdS + Vdp \quad \left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p$$

$$dA = -pdV - SdT \quad \left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

$$dG = Vdp - SdT \quad \left(\frac{\partial V}{\partial T} \right)_p = - \left(\frac{\partial S}{\partial p} \right)_T$$

$$dz = gdx + hdy$$

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

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

$$\left(\frac{\partial g}{\partial y} \right)_x = \left(\frac{\partial h}{\partial x} \right)_y$$

Maxwell relations



5.1 Properties of the internal energy

$$dU = TdS - pdV$$

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

$$\left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

$$dH = TdS + Vdp$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial H}{\partial S}\right)_p = T, \quad \left(\frac{\partial H}{\partial p}\right)_S = V$$

$$dA = -pdV - SdT$$

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

$$\left(\frac{\partial A}{\partial V}\right)_T = -p, \quad \left(\frac{\partial A}{\partial T}\right)_V = -S$$

$$dG = Vdp - SdT$$

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

$$\left(\frac{\partial G}{\partial p}\right)_T = V, \quad \left(\frac{\partial G}{\partial T}\right)_p = -S$$



5.1 Properties of the internal energy

2). The variation of internal energy with volume

The internal pressure is defined as $\pi_T = \left(\frac{\partial U}{\partial V} \right)_T$

$$\text{Since } dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV$$

If divide both sides of equation by dV with the constraint of constant T

$$\left(\frac{\partial U}{\partial V} \right)_T = \left(\frac{\partial U}{\partial S} \right)_V \left(\frac{\partial S}{\partial V} \right)_T + \left(\frac{\partial U}{\partial V} \right)_S$$



5.1 Properties of the internal energy

2). The variation of internal energy with volume

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_S \leftarrow \left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

$$= T \left(\frac{\partial S}{\partial V}\right)_T - p \quad \leftarrow \quad \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$= T \left(\frac{\partial p}{\partial T}\right)_V - p$$

Therefore:

$$\underline{\pi_T = T \left(\frac{\partial p}{\partial T}\right)_V - p}$$



Example - Deriving a thermodynamic relation

Show thermodynamically that $\pi_T = 0$ for a perfect gas, and compute its value for a van der Waals gas

Method: Proving a result 'thermodynamically' means basing it entirely on general thermodynamic relations and equations of state.

Answer: 1). For a perfect gas, $pV = nRT$, and

$$\left(\frac{\partial p}{\partial T}\right)_V = nR / V$$

From the equation of $\pi_T = T \left(\frac{\partial p}{\partial T}\right)_V - p$

$$\pi_T = \frac{nRT}{V} - p = 0$$



Example 5.1 Deriving a thermodynamic relation

2). The equation of state of a van der Waals gas is

$$p = \frac{nRT}{V - nb} - a \frac{n^2}{V^2} \quad \longrightarrow \quad \left(\frac{\partial p}{\partial T} \right)_V = \frac{nR}{V - nb}$$

That is

$$\begin{aligned} \pi_T &= T \left(\frac{\partial p}{\partial T} \right)_V - p \\ &= \frac{nRT}{V - nb} - \frac{nRT}{V - nb} + a \frac{n^2}{V^2} \\ &= a \frac{n^2}{V^2} \end{aligned}$$



5. The Second Law: the machinery

Combing the First and Second Laws

5.1 Properties of the internal energy

5.2 Properties of the Gibbs energy



5.3 The chemical potential of a pure substance

Real gases:the fugacity

5.4 The definition of fugacity

5.5 Standard states of real gases

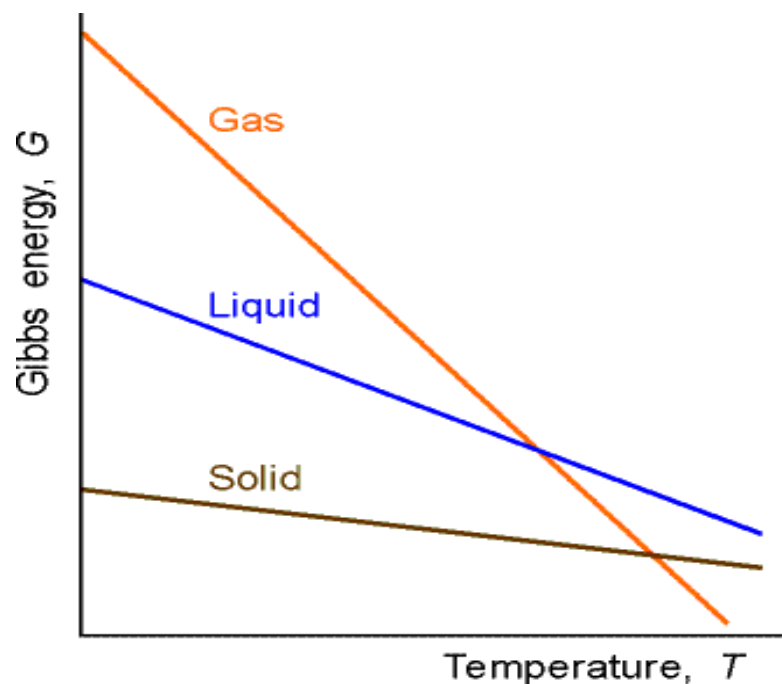
5.6 The relation between fugacity and pressure



5.2 Properties of the Gibbs energy

1). The outline of the Gibbs energy with T and p

$$G = G(p, T) \quad dG = Vdp - SdT \quad \left(\frac{\partial G}{\partial T}\right)_p = -S$$



The variation of the Gibbs energy with the temperature is determined by the entropy

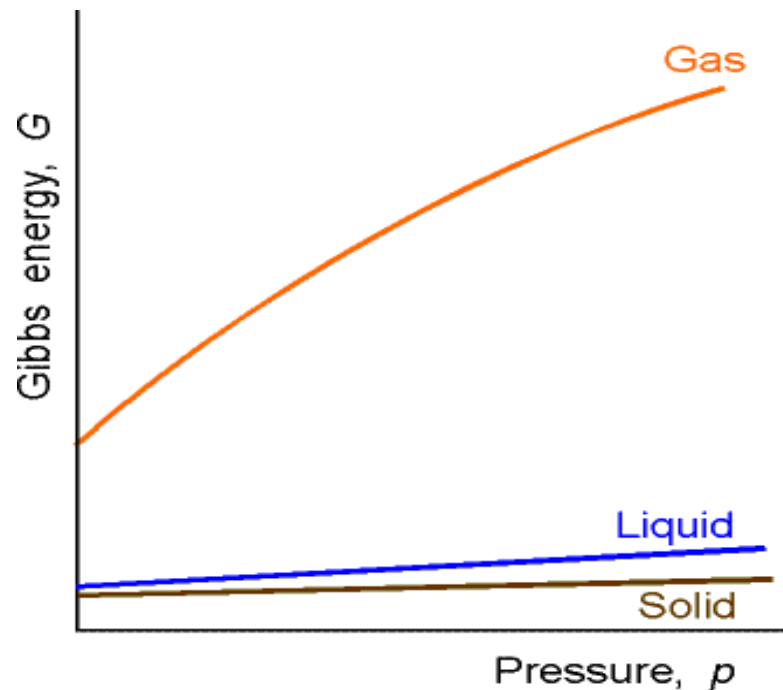
The entropy of the gaseous phase of a substance is greater than that of the liquid phase, and the entropy of the solid phase is smallest, the **Gibbs energy** changes most steeply for the **gas phase**, followed by the liquid phase, and then the solid phase of the substance.



5.2 Properties of the Gibbs energy

1). The outline of the Gibbs energy with T and p

$$G = G(p, T) \quad dG = Vdp - SdT \quad \left(\frac{\partial G}{\partial p} \right)_T = V$$



The variation of the Gibbs energy with the pressure determined by the volume of the sample

The volume of the gaseous phase of a substance is greater than that of the same amount of liquid phase, and the volume of the solid phase is smallest, the Gibbs energy changes most steeply for the gas phase, followed by the liquid phase, and then the solid phase of the substance.



Example - Calculating the effect of pressure on the Gibbs energy

- Calculate the change in the molar Gibbs energy of:**
- (a) liquid water treated as an incompressible fluid ,and**
 - (b) water vapour treated as a perfect gas, when the pressure is increased isothermally from 1.0 bar to 2.0 bar at 298 K.**



Example - Calculating the effect of pressure on the Gibbs energy

Method: In each case, the change in molar Gibbs energy can be obtained by integration of the equation $dG = Vdp - SdT$ with the temperature held constant:

$$G_m(p_f) - G_m(p_i) = \int_{p_i}^{p_f} V_m dp$$



Example- Calculating the effect of pressure on the Gibbs energy

Answer:

(a) For an incompressible fluid, the molar volume is independent of the pressure so V_m can be treated as a constant. For the incompressible liquid, V_m is constant at $18.0 \text{ cm}^3\text{mol}^{-1}$, then

$$\begin{aligned} G_m(p_f) - G_m(p_i) &= V_m \int_{p_i}^{p_f} dp = V_m \times (p_f - p_i) \\ &= (18.0 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) \times (1.0 \times 10^5 \text{ Pa}) \\ &= +1.8 \text{ Pa m}^3 \text{ mol}^{-1} = +1.8 \text{ J mol}^{-1} \end{aligned}$$



Example - Calculating the effect of pressure on the Gibbs energy

Answer:

(b) For a perfect gas, the molar volume varies with pressure as $V_m = RT/p$, so this expression must be used in the integrand, and the integration performed treating RT as a constant:

$$\begin{aligned}G_m(p_f) - G_m(p_i) &= \int_{p_i}^{p_f} \frac{RT}{p} dp = RT \ln \left(\frac{p_f}{p_i} \right) \\ &= (2.48 \text{ kJ mol}^{-1}) \times \ln 2.0 \\ &= +1.7 \text{ kJ mol}^{-1}\end{aligned}$$



Example - Calculating the effect of pressure on the Gibbs energy

(a) For an incompressible

$$G_m(p_f) - G_m(p_i) = +1.8 \text{ Jmol}^{-1}$$

(b) For a perfect gas

$$G_m(p_f) - G_m(p_i) = +1.7 \text{ kJmol}^{-1}$$



5.2 Properties of the Gibbs energy

2). The temperature dependence of the Gibbs energy

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$G = H - TS \quad \downarrow$$

$$S = (H - G) / T$$

$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G - H}{T}$$

$$\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} = -\frac{H}{T}$$

$$\left(\frac{\partial}{\partial T} \left(\frac{G}{T}\right)\right)_p = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p + G \frac{d}{dT} \frac{1}{T}$$

$$= \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2}$$

$$= \frac{1}{T} \left\{ \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} \right\}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_p$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial G}{\partial V}\right)_T$$

$$V = \left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T$$

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



5.2 Properties of the Gibbs energy

2). The temperature dependence of the Gibbs energy

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

the Gibbs-Helmholtz ($G-H$) equation

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

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

$$p = - \left(\frac{\partial U}{\partial V} \right)_S = \left(\frac{\partial A}{\partial V} \right)_T$$


$$V = \left(\frac{\partial H}{\partial p} \right)_S = \left(\frac{\partial G}{\partial p} \right)_T$$

$$S = - \left(\frac{\partial A}{\partial T} \right)_V = \left(\frac{\partial G}{\partial T} \right)_p$$



5.2 Properties of the Gibbs energy

2). The temperature dependence of the Gibbs energy

$$\begin{aligned}\left(\frac{\partial(\mathbf{G}/T)}{\partial T}\right)_p &= \left(\frac{\partial(\mathbf{G}/T)}{\partial(1/T)}\right)_p \frac{d(1/T)}{dT} \\ &= \left(\frac{\partial(\mathbf{G}/T)}{\partial(1/T)}\right)_p \times \left(-\frac{1}{T^2}\right) \\ &= \mathbf{H} \times \left(-\frac{1}{T^2}\right)\end{aligned}$$

$$\mathbf{H} = \left(\frac{\partial(\mathbf{G}/T)}{\partial(1/T)}\right)_p$$

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

$$p = -\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T$$

$$V = \left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_p$$



5.2 Properties of the Gibbs energy

3). The pressure dependence of the Gibbs energy

At constant temperature: $(dG = Vdp - SdT)$

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp$$

For a liquid or solid, the volume changes only slightly as the pressure changes, so V may be treated as a constant. For molar quantities:

$$\begin{aligned} G_m(p_f) &= G_m(p_i) + V_m(p_f - p_i) \\ &= G_m(p_i) + V_m \Delta p \end{aligned}$$

At normal lab. conditions $V_m \Delta p$ is small, so it suggests that the G of solid and liquid are independent of p .



5.2 Properties of the Gibbs energy

3). The pressure dependence of the Gibbs energy

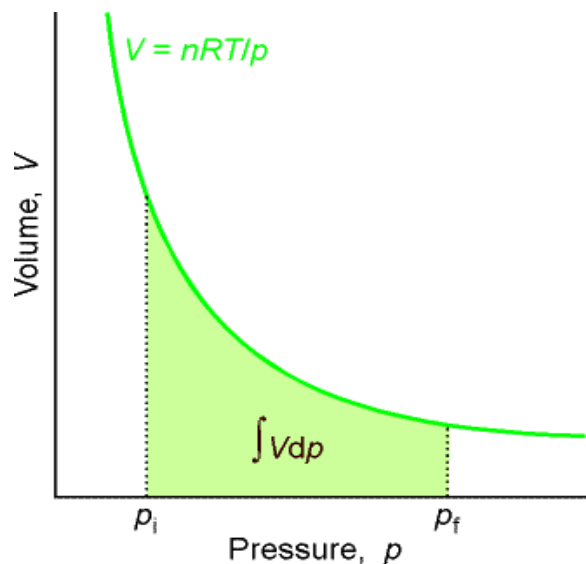
For a perfect gas, the Gibbs energy may depend strongly on the pressure; and the volume also varies markedly with the pressure. Then $V = nRT/p$:

$$\begin{aligned}G(p_f) &= G(p_i) + V \int_{p_i}^{p_f} dp \\&= G(p_i) + nRT \int_{p_i}^{p_f} \frac{dp}{p} \\&= G(p_i) + nRT \ln \left(\frac{p_f}{p_i} \right)\end{aligned}$$



5.2 Properties of the Gibbs energy

3). The pressure dependence of the Gibbs energy



$$G(p_f) = G(p_i) + nRT \ln \left(\frac{p_f}{p_i} \right)$$

If set $p_i = p^\ominus$ then the Gibbs energy of a perfect gas at a pressure p is related to its standard value by

$$G(p) = G^\ominus + nRT \ln \left(\frac{p}{p^\ominus} \right)$$



Example

Calculate the change in the molar Gibbs energy of hydrogen when its pressure is increased isothermally from 1.0 atm to 100.0 atm at 298K.



Example

Answer:

1.00mol hydrogen (id.g)

298K, 1.0atm, V_1

ΔG

1.00mol hydrogen (id.g)

298K, 100.0atm, V_2

$$G(p_f) = G(p_i) + nRT \ln \left(\frac{p_f}{p_i} \right)$$

$$\begin{aligned} \Delta G_m &= RT \ln \left(\frac{p_f}{p_i} \right) \\ &= (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln \left(\frac{100.00 \text{ atm}}{1.00 \text{ atm}} \right) \\ &= 11.41 \text{ kJmol}^{-1} \end{aligned}$$



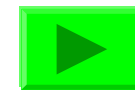
5. The Second Law: the machinery

Combing the First and Second Laws

5.1 Properties of the internal energy

5.2 Properties of the Gibbs energy

5.3 The chemical potential of a pure substance



Real gases:the fugacity

5.4 The definition of fugacity

5.5 Standard states of real gases

5.6 The relation between fugacity and pressure



5.3 The chemical potential of a pure substance

1) Partial molar quantities

V, U, H, S, A and G (general X) are extensive properties. X depends on not only T and p , but also n .

For a single phase system of a pure substance, X_m is certain when T and p are specific

$$X = nX_m$$

For a mixture of pure substances at constant T and p

$$X = n_1 X_{m,1} + n_2 X_{m,2} + \dots$$



5.3 The chemical potential of a pure substance

Substance 1	Substance 2	Mixture
n_1	n_2	$n_2 + n_1$
T, p	T, p	T, p
$V_1 = n_1 V_{m,1}$	$V_2 = n_2 V_{m,2}$	V
$U_1 = n_1 U_{m,1}$	$U_2 = n_2 U_{m,2}$	U
$H_1 = n_1 H_{m,1}$	$H_2 = n_2 H_{m,2}$	H
$S_1 = n_1 S_{m,1}$	$S_2 = n_2 S_{m,2}$	S
$A_1 = n_1 A_{m,1}$	$A_2 = n_2 A_{m,2}$	A
$G_1 = n_1 G_{m,1}$	$G_2 = n_2 G_{m,2}$	G

?

For perfect gases, $\Delta V = \Delta U = \Delta H = 0$; $\Delta S \neq 0$, nor ΔA or ΔG .

For real gases, the change in extensive properties in a mixture is generally $\Delta X \neq 0$.



5.3 The chemical potential of a pure substance

1) Partial molar quantities

Generally, $X = f(T, p, n_1, n_2, \dots)$, and

$$dX = \left(\frac{\partial X}{\partial T} \right)_{p, n_1, n_2, \dots} dT + \left(\frac{\partial X}{\partial p} \right)_{T, n_1, n_2, \dots} dp + \left(\frac{\partial X}{\partial n_1} \right)_{T, p, n_2, n_3, \dots} dn_1 + \dots$$

$\left(\frac{\partial X}{\partial n_i} \right)_{T, p, n_j}$ the partial molar quantity

Note that: 1) X , extensive properties
2) at constant T and p



5.3 The chemical potential of a pure substance

1) Partial molar quantities

$$V_i = \left(\frac{\partial V}{\partial n_i} \right)_{T,p,n_j} \quad U_i = \left(\frac{\partial U}{\partial n_i} \right)_{T,p,n_j} \quad S_i = \left(\frac{\partial S}{\partial n_i} \right)_{T,p,n_j}$$

$$G_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j}$$

The chemical potential of component i in the mixture.



5.3 The chemical potential of a pure substance

2) The definition of chemical potential of a pure substance

The chemical potential, μ , of a pure substance is defined as

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{T,p}$$

For a pure substance, the Gibbs energy is $G = nG_m$

$$\mu = \left(\frac{\partial nG_m}{\partial n} \right)_{T,p} = G_m$$

The chemical potential, μ , is the same as the molar Gibbs energy G_m .



5.3 The chemical potential of a pure substance

3) The chemical potential

$$\left(\frac{\partial G_m}{\partial p} \right)_T = V_m$$

$$dG_m = V_m dp \quad \mu = G_m$$

$$d\mu = V_m dp$$



5.3 The chemical potential of a pure substance

$$\underline{d\mu = V_m dp}$$

For a perfect gas: $V_m = \frac{RT}{p}$

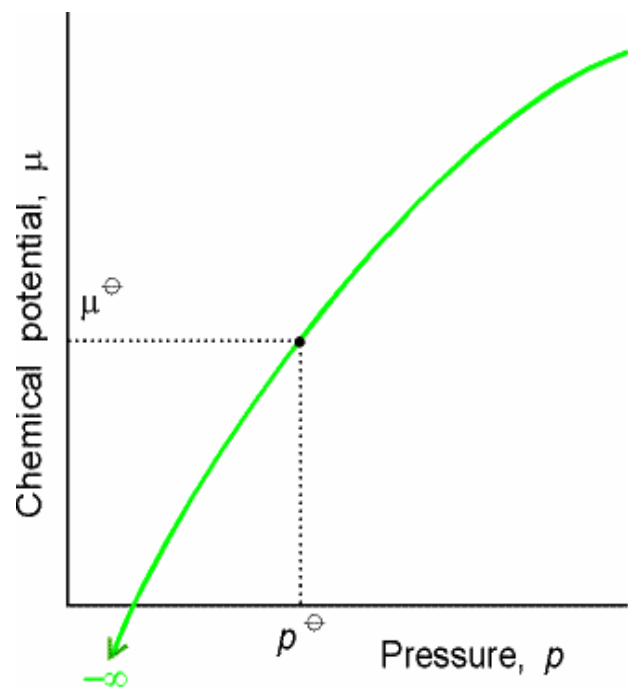
$$d\mu = RT \frac{dp}{p}$$

Let μ^\ominus denotes the standard chemical potential, the molar Gibbs energy of the pure gas at $(1 \text{ bar})p^\ominus$

$$\mu = \mu^\ominus + RT \ln \left(\frac{p}{p^\ominus} \right)$$



5.3 The chemical potential of a pure substance



$$\mu = \mu^{\ominus} + RT \ln \left(\frac{p}{p^{\ominus}} \right)$$

The chemical potential, μ , of a perfect gas is proportional to $\ln p$, and the standard state is reached at p^{\ominus} . Note that, as $p \rightarrow 0$, μ becomes negatively infinite.

The variation of chemical potential of a perfect gas with p



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Real gases:the fugacity

5.4 The definition of fugacity

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Real gases: the fugacity

At various stages in the development of physical chemistry it is necessary to switch from consideration of idealized systems to real systems. In many cases it is desirable to preserve the form of the expressions that have been derived for the idealized system. Then deviations from the idealized behavior can be expressed most simply. We shall illustrate such procedure in this section by considering how the expressions that have been derived for perfect gases, particularly the equation for the chemical potential of a perfect gas, are adapted to describe real gases.



5.4 The definition of fugacity

The chemical potential of a perfect gas:

$$\mu = \mu^{\ominus} + RT \ln \left(\frac{p}{p^{\ominus}} \right)$$

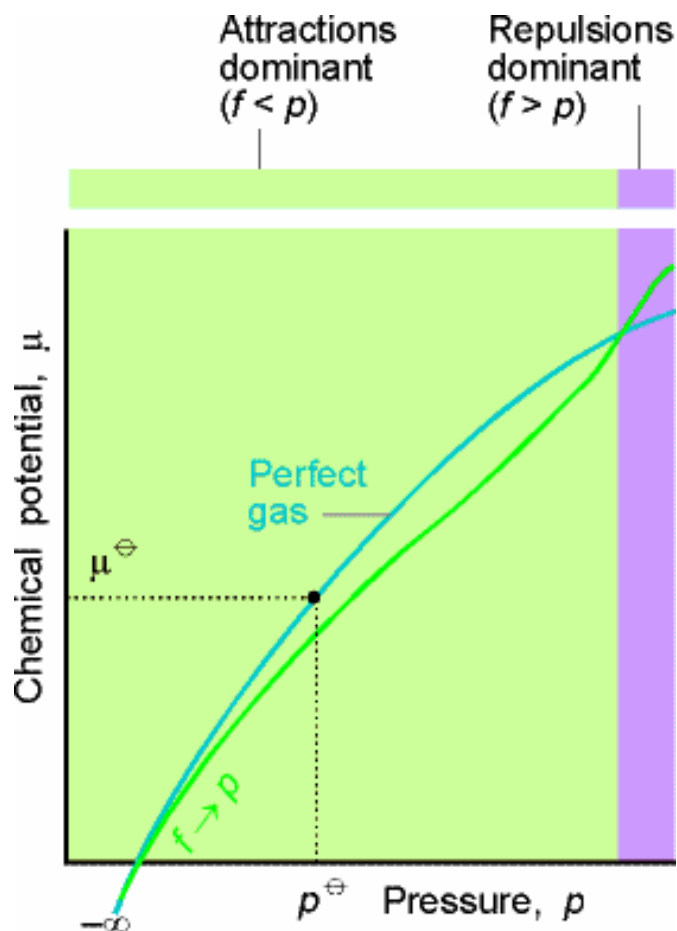
For a real gas, replace the true pressure, p , by an effective pressure, f , then the fugacity of a real gas is defined as:

$$\mu = \mu^{\ominus} + RT \ln \left(\frac{f}{p^{\ominus}} \right)$$

The name 'fugacity' comes from the Latin for 'fleetness' in the sense of 'escaping tendency'. Fugacity has the same dimension as pressure.



5.4 The definition of fugacity



The μ of a real gas

For the chemical potential of a real gas:

- at higher p , $\mu_{\text{real}} > \mu_{\text{perfect}}$
the repulsive forces are dominant and the 'escaping tendency' is increased.
- at lower p , $\mu_{\text{real}} < \mu_{\text{perfect}}$
the attractive forces are dominant and the molecules have a lower 'escaping tendency'.
- as $p \rightarrow 0$, μ coincides with the value for a perfect gas.



5.5 Standard states of real gases

A perfect gas is in its standard state when its pressure is (1 bar): the pressure arises solely from the kinetic energy of the molecules and there are no intermolecular forces to take into account.

The standard state of a real gas is a hypothetical state in which the gas is at a pressure p^\ominus and behaving perfectly.

$$d\mu = V_m dp \quad \mu = \mu^\ominus + RT \ln \left(\frac{f}{p^\ominus} \right)$$



5.6 The relation between fugacity and pressure

The fugacity coefficient, φ , is defined as:

$$\varphi = \frac{f}{p} \quad \text{or} \quad f = \varphi p$$

The fugacity coefficient, φ

- 1). Dimensionless;
- 2). depends on the identity of the gas, the pressure, and the temperature.

$$\mu = \mu^\ominus + RT \ln \left(\frac{f}{p^\ominus} \right) = \mu^\ominus + RT \ln \left(\frac{\varphi p}{p^\ominus} \right)$$



5.6 The relation between fugacity and pressure

In terms of fugacity coefficient:

$$\mu = \mu^\ominus + RT \ln \left(\frac{p}{p^\ominus} \right) + RT \ln \phi$$

The terms of the μ^\ominus and $\ln \frac{p}{p^\ominus}$ are the same as those in the above equation. Therefore, the $RT \ln \phi$ must express the entire effect of all intermolecular forces.

For all gases, $f = p$ as $p \rightarrow 0$, $\lim_{p \rightarrow 0} \frac{f}{p} = 1$

For a perfect gas: $f = p$ and $\phi = 1$; for a real gas: $f \neq p$ and $\phi \neq 1$. ϕ is a measure of a real gas derived from the perfect gas.



5.6 The relation between fugacity and pressure

The equation $d\mu = V_m dp$ is true for all gases. Let f denotes the fugacity when the pressure is p and f' the fugacity when the pressure is p' , from the definition of fugacity we have:

$$\mu = \int_{p^\ominus}^f V_m dp = \mu^\ominus + RT \ln \left(\frac{f}{p^\ominus} \right)$$

$$\mu' = \int_{p^\ominus}^{f'} V_m dp = \mu^\ominus + RT \ln \left(\frac{f'}{p^\ominus} \right)$$



5.6 The relation between fugacity and pressure

$$\int_{p'}^p V_m dp = \mu - \mu' = RT \ln \left(\frac{f}{f'} \right)$$

If the gas were perfect:

$$\int_{p'}^p V_{\text{perfect}, m} dp = \mu_{\text{perfect}} - \mu'_{\text{perfect}} = RT \ln \left(\frac{p}{p'} \right)$$

The difference of the two equations is:

$$\int_{p'}^p (V_m - V_{\text{perfect}, m}) dp = RT \left\{ \ln \left(\frac{f}{f'} \right) - \ln \left(\frac{p}{p'} \right) \right\}$$



5.6 The relation between fugacity and pressure

$$\ln \left(\frac{f}{p} \times \frac{p'}{f'} \right) = \frac{1}{RT} \int_{p'}^p (V_m - V_{\text{perfect, m}}) dp$$

When $p' \rightarrow 0$, the gas behaves perfectly and f' becomes equal to the pressure p' . Therefore, $p'/f' \rightarrow 1$ as $p' \rightarrow 0$. If we take this limit, this equation becomes:

$$\ln \left(\frac{f}{p} \right) = \frac{1}{RT} \int_0^p (V_m - V_{\text{perfect, m}}) dp$$

With $\varphi = f/p$



5.6 The relation between fugacity and pressure

At a general pressure p , the fugacity coefficient of a gas is given by:

$$\ln \phi = \int_0^p \left(\frac{Z - 1}{p} \right) dp$$

$$\mu = \mu^\ominus + RT \ln \left(\frac{p}{p^\ominus} \right) + RT \ln \phi$$

where Z is the compression factor of the gas. This equation is an explicit expression for the **fugacity coefficient** at any pressure p . The fugacity of the gas at that pressure can be obtained by $f = \phi p$



Real gases: the fugacity


$$\ln \varphi = \int_0^p (Z - 1) \frac{dp}{p}$$

If $Z < 1$ throughout the range of integration:

The integrand < 0 , $\varphi < 1$,  $f < p$,

The molecules tend to stick together and the chemical potential of the gas is less than that of a perfect gas;

If $Z > 1$ throughout the range of integration (higher pressure):

The integrand > 0 , $\varphi > 1$,  $f > p$,

The repulsive interactions are dominant and tend to drive the particles apart, and the chemical potential of the gas is greater than that of a perfect gas



Real gases: the fugacity

The expression for chemical potential:

$$d\mu = dG_m = V_m dp$$

The chemical potential of a perfect gas :

$$\mu = \mu^\ominus + RT \ln \left(\frac{p}{p^\ominus} \right)$$

The chemical potential of a real gas and the fugacity, f :

$$\mu = \mu^\ominus + RT \ln \left(\frac{f}{p^\ominus} \right) = \mu^\ominus + RT \ln \left(\frac{p}{p^\ominus} \right) + RT \ln \varphi$$

The fugacity coefficient, $\varphi(f,p)$, $\varphi(Z,p)$:

$$\varphi = f/p \quad \text{or} \quad f = \varphi p \quad \ln \varphi = \int_0^p (Z - 1) \frac{dp}{p}$$



Example - Calculating a fugacity

Suppose that the attractive interactions between gas particles can be neglected, and find an expression for the fugacity of a van der Waals gas in terms of the pressure. Estimate its value for ammonia at 10.00 atm and 298.15 K.




Example - Calculating a fugacity

Method: The starting point for the calculation is equation

$$\ln \phi = \int_0^p \left(\frac{Z - 1}{p} \right) dp$$

Answer: the van der Waals equation is as followings:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$



$$p = \frac{RT}{V_m - b} \quad \longrightarrow \quad pV_m = RT + bp$$

and

$$Z = \frac{pV_m}{RT}$$

hence

$$Z = 1 + \frac{bp}{RT}$$



Example - Calculating a fugacity

$$\begin{aligned}\ln \varphi &= \int_0^p \left(\frac{Z-1}{p} \right) dp \\ &= \int_0^p \left(\frac{b}{RT} \right) dp = \frac{bp}{RT}\end{aligned}$$

$$\varphi = e^{bp/RT} \quad \varphi = f/p$$

$$\underline{f = \varphi p = p e^{bp/RT}}$$

For ammonia at 10.00 atm and 298.15 K

$$f = (10.00 \text{ atm}) \times e^{0.01515} = 10.2 \text{ atm}$$



Example

The fugacity coefficient of a certain gas at 290 K and 2.1MPa is 0.68. Calculate the difference of its chemical potential from that of a perfect gas in the same state.

Method:

$$\mu^{\text{id}} = \mu^{\ominus} + RT \ln \left(\frac{p}{p^{\ominus}} \right) \quad \mu = \mu^{\ominus} + RT \ln \left(\frac{f}{p^{\ominus}} \right)$$



$$\mu - \mu^{\text{id}} = RT \ln \frac{f}{p} = RT \ln \phi \quad \leftarrow \quad \phi = \frac{f}{p}$$



Example

Answer:

$$\begin{aligned}\mu - \mu^{\text{id}} &= RT \ln \phi \\ &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (290 \text{ K}) \times \ln(0.68) \\ &= -930 \text{ J mol}^{-1}\end{aligned}$$



Example

Consider a system consisting of 1.5 mol CO_2 (g), initially at 15°C and 9.0 atm and confined to a cylinder of cross-section 100.0 cm^2 . The sample is allowed to expand adiabatically against an external pressure of 1.5 atm until the piston has moved outwards through 15 cm. Assume that carbon dioxide may be considered a perfect gas with $C_{V,m} = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$, and calculate (a) q , (b) w , (c) ΔU , (d) ΔT , and (e) ΔS .



Example

Method and answer:

(a). q : (adiabatic) $\rightarrow q = 0$

(b). w : $w = -p_{\text{ex}}\Delta V$ \downarrow

$$w = -(1.5\text{atm}) \times \frac{1.01 \times 10^5 \text{ Pa}}{\text{atm}} \times (100\text{cm}^2) \times (15\text{cm}) \times \frac{1\text{m}^3}{10^6 \text{ cm}^3}$$
$$= -227.2 \text{ J}$$

(c). ΔU : $\Delta U = q + w = -227.2\text{J}$



Example

$$(d). \Delta T: \left(\frac{\partial U}{\partial T} \right)_V = C_V \quad \Delta U = nC_{V,m} \Delta T$$



$$\Delta T = \frac{\Delta U}{nC_{V,m}}$$

$$= \frac{-227.2\text{J}}{(1.5\text{mol}) \times (28.8\text{JK}^{-1}\text{mol}^{-1})}$$

$$= -5.28 \text{ K}$$



Example

$$T_f = T_i + \Delta T = 288.15\text{K} - 5.28\text{K} = 282.9\text{K}$$

$$\begin{aligned} V_i &= \frac{nRT_i}{p_i} \\ &= \frac{(1.5\text{atm}) \times (8.206 \times 10^{-2} \text{LatmK}^{-1}\text{mol}^{-1}) \times 288.2\text{K}}{9.0 \text{ atm}} = 3.942\text{L} \end{aligned}$$

$$V_f = V_i + \Delta V = 3.942\text{L} + 100\text{cm}^2 \times (15\text{cm}) \times \left(\frac{1\text{L}}{1000\text{cm}^3} \right) = 5.44 \text{ L}$$

$$\Delta S = 3.2 \text{ J K}^{-1}$$



Part 1: Equilibrium

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