# CHM 304 – Thermodynamics (Revised)

## First law of thermodynamics

### Introduction

Scope of thermodynamics, system and surrounding/universe, states and state functions. Thermodynamic variables.

Expansion or pdv work. Relationships between ΔE, ΔH and q. Common thermodynamics problems – partial derivatives of heat capacities ($C_p$ and $C_v$) and relationships heat capacities of gas, liquid and solid. Thermochemistry – temperature dependence of enthalpy, Kirchoff's law. Application of first law of thermodynamics to (a) ideal gases (b) real gases.

## Second law of Thermodynamics

### Introduction

Need to study the second law. Mathematical statement of second law – Carnot cycle, Carnot theorem. Entropy of a system – Isothermal, adiabatic, isobaric and isochoric changes and calculations. Entropy of irreversible processes, carnot refrigerator.

Free Energy function, Pressure and temperature coefficients of free energy (ΔG) and equilibrium constant, ΔG and ΔH relationship, Variation of equilibrium constant, K, with temperature, ΔG and maximum work, ΔG and electrical work, Clapeyron, Classius-Clapeyron, Gibbs-Helmholtz equation equations.

## Third law of Thermodynamics - Entropy at absolute zero temperature and total entropy of phase changes

Application of Thermodynamic concepts to mixtures and solutions; Entropy, enthalpy, and free energy of mixing, Open system and Chemical potential, Chemical potential of ideal gas mixture or solution, Fugacity function, Partial molar quantities – Gibbs-Duhem equation, Phase rule and phase diagrams, Ideal binary mixtures – Rauolt's and Henry's laws, Solubility and Pressure, Solubility and temperature, Solutions of involatile solutes – The colligative properties, Colligative properties of electrolytes

## The First Law of Thermodynamics

There are several word statements of the first law of thermodynamics:

Energy is conserved.

(Which is another way of saying that energy cannot be created or destroyed. You can change its form, but you cannot create it or destroy it.)

It is impossible to make a perpetual motion machine of the first kind.

(A perpetual motion machine of the first kind is a system that gives energy to the surroundings, but produces no change in the system itself and no other change to the surroundings. This statement implies that there is a perpetual motion machine of the second kind. We will find out about a perpetual motion machine of the second kind when we meet the second law of thermodynamics.)

The mathematical statement of the first law is phrased in terms of a process. Given any change or process,

$$\text{initial state} \rightarrow \text{final state}$$

$$\Delta U = U_{\text{final}} - U_{\text{initial}} ,$$

or

$$\text{state 1} \rightarrow \text{state 2}$$

$$\Delta U = U_2 - U_1 .$$

(Initial and final states must both be at equilibrium.)

Then the first law of thermodynamics says that

$$\Delta U = q + w.$$

The first law of thermodynamics is a law of observation. No one has ever observed a situation where energy is not conserved so we elevate this observation to the status of a law. The real justification of this comes when the things we derive using the first law turn out to be true - that is, verified by experiment.

(Actually there are situations were energy is not conserved. We now know that in processes where the nuclear structure of matter is altered mass can be converted into energy and vice versa. This is a consequence of special relativity were it is found that matter has a "rest energy," $mc^2$, where $m$ is the mass to be converted to energy and $c$ is the speed of light. As a consequence of nuclear energy we should say that, Energy + the energy equivalent of mass is conserved.

Then the first law would be written,

$$\Delta U = q + w + \Delta mc^2.$$

For chemical processes the change in energy due to changes in mass is negligible - though not zero - so we can ignore it.)

The first law can be written in differential form,

$$dU = dq + dw$$

Which is called the differential form of the first law.

(Actually, this is the differential form of the first law for a closed system, that is, for a system in which no material moves in or out of the system. Later we will write the differential form of the first law for an open system, where material can move in or out of the system.)

Note: Some writers like to use a special symbol for the *d* in *dq* and *dw* to indicate that these differentials are not in the same mathematical class as, for example, *dU*. We will not use this notation. As soon as we have learned what the difficulty is with the present *d* you will be expected just to remember that the *d* in *dq* and *dw* is different than the *d* in *dU*.

## pV Work

We have seen that the expression for work must be obtained from physics. The expression for mechanical work, force times distance, is given by,

$$dw = fdx,$$

or, for a finite change,

$$w = \int_{x_1}^{x_2} f(x)dx.$$

We would now like to apply these expressions for mechanical work to the case where work is accomplished by the expansion or contraction of a system under an external pressure.

Let us consider a cylinder of cross-sectional area $A$ fitted with a piston. The apparatus is arranged so that the piston encloses a sample at pressure $p_{\text{int}}$, and the piston is attached to a mechanism which will maintain an external pressure, $p_{\text{ext}}$, in the apparatus. We will assume that $p_{\text{int}} \geq p_{\text{ext}}$.

It turns out that it is easier to calculate the work done on the surroundings, $w'$. (Recall that $w' = -w$.) In this case,

$$dw' = fdx. \qquad (1)$$

The piston is released to move a distance $dx$. Since pressure is force per unit area, the force against which the piston moves is $p_{\text{ext}} A$. So the work, $dw'$ is
$dw' = fdx = p_{ext} Adx$.  (2)
But $Adx$ is a differential volume swept out by the piston in the expansion. Call the differential volume $Adx = dV$. Then
$dw' = fdx = p_{ext} Adx = p_{\text{ext}} dV$.  (3)
Going back to work done on the system, $dw$, we find,
$dw = -\, dw' = -p_{\text{ext}} dV$.  (4)

## Reversible and Irreversible Processes

A reversible process is one that can be halted at any stage and reversed. In a reversible process the system is at equilibrium at every stage of the process. An irreversible process is one where these conditions are not fulfilled.

If $p_{\text{int}} > p_{\text{ext}}$ in an expansion process then the process is irreversible because the system does not remain at equilibrium at every stage of the process. (There will be turbulence and temperature gradients, for example.) For irreversible processes, $pV$ work must be calculated using

$dw = -\, p_{\text{ext}} dV$.  (5)
On the other hand, if $p_{\text{int}} = p_{\text{ext}}$ then the process can be carried out reversibly. Also, there is then no need to distinguish between external pressure and internal pressure so that
$p_{\text{int}} = p_{\text{ext}} = p$
and there is only one pressure defined for the system. In this case, which will account for the majority of problems that we deal with,
$dw = -\, pdV$,  (6)
and

$$w = -\int_{V_1}^{V_2} p\, dV. \qquad (7)$$

## Example Calculations

First example: A reversible expansion with $dp = 0$. That is, a process at constant pressure.

We write our expression for reversible work done on the system,

$$w = -\int_{V_1}^{V_2} p\, dV. \qquad (7)$$

If pressure is constant then the $p$ can be brought outside the integral to give,

$$
\begin{aligned}
w &= -\int_{V_1}^{V_2} p\,dV \\
&= -p\int_{V_1}^{V_2} dV \\
&= -p(V_2 - V_1) \\
&= -p\Delta V.
\end{aligned}
$$

(8, a, b, c, d)

(The answer will come out in Latm and should be converted to J using 1 Latm = 101.325 J.

Second example: An isothermal reversible expansion. That is, $dT = 0$. We use the same starting place

$$w = -\int_{V_1}^{V_2} p\,dV,$$

(7)

but this time pressure is not constant and will change as $V$ changes,

$$w = -\int_{V_1}^{V_2} p(V)\,dV.$$

(9)

In order to do the integration we must know how pressure varies with volume. We can obtain this information from the equation of state. If our substance is a gas we can get an approximate value of the expansion work using the ideal gas equation of state, where

$$p = \frac{nRT}{V}.$$

(10)

Substituting the ideal gas expression for pressure into Equation (7) we get

$$w = -\int_{V_1}^{V_2} \frac{nRT}{V}\,dV.$$

(11)

This time $T$ is constant so that we can bring the $nRT$ outside the integral to get.

$$w = -nRT\int_{V_1}^{V_2} \frac{1}{V}\,dV,$$

(12)

Which integrates to give

$$
\begin{aligned}
w &= -nRT(\ln V_2 - V_1) \\
&= -nRT\ln\frac{V_2}{V_1}.
\end{aligned}
$$

(13a, b)

The next best approximation would be to approximate the volume dependence of the pressure using the van der Waals equation of state.

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}.$$

We will leave it as an exercise for the reader to calculate the expansion work for a van der Waals gas.

A better approximation yet could be obtained using the virial expansion to give the volume dependence of pressure,

$$p = \frac{nRT}{V}\left(1 + \frac{B(T)n}{V} + \frac{C(T)n^2}{V^2} + \cdots\right).$$

The General Case

Suppose we go from $p_1V_1$ to $p_2V_2$ by some general path. The reversible work is still represented by Equation (7),

$$w = -\int_{V_1}^{V_2} p\,dV. \qquad (7)$$

The path from $p_1V_1$ to $p_2V_2$ can be represented by a curve on a $p$-$V$ diagram.

The integral in Equation (7) can be represented by the area under the curve which goes from $p_1V_1$ to $p_2V_2$, so that the work becomes,

$w = -$ area.

Notice that there are many possible curves which would connect the points $p_1V_1$ and $p_2V_2$ and each curve would have a different area and give a different value for $w$. We conclude that $w$ depends on the path, unlike ΔU which only depends on the initial and final states. We call variables like $U$, $p$, $V$, $T$, and so on, **state variables** because $\Delta U$, $\Delta p$, $\Delta V$, $\Delta T$, and so on, do not

depend on the path, but only on the initial and final states of the system. A quantity like *w* which does depend on path is not a state variable. We will never write *w* with a Δ in front of it.
We will soon see that *q* is also path dependent.

## Heat and Heat Capacity

If we add heat to a sample of material, often the temperature will increase. (If we are at the temperature of a phase change, for example ice in water, the temperature will not change it will just melt some of the ice.) Away from a phase change adding heat will always give an increase in temperature. The amount of the temperature increase depends on how much heat was added, the size of the sample, the original temperature of the sample, and on how the heat was added. The two obvious choices on how to add the heat are to add it holding volume constant or to add it holding pressure constant. (There may be other choices, but they will not concern us.)

Let's assume for the moment that we are going to add heat to our sample holding volume constant, that is, $dV = 0$. Let $q_V$ be the heat added[1] (the subscript, $V$, indicates that the heat is being added at constant $V$). Also, let $\Delta T$ be the temperature change. The ratio, $\frac{q_V}{\Delta T}$, depends on the material, the amount of material, and the temperature. In the limit where $q_V$ goes to zero (so that $\Delta T$ also goes to zero) this ratio becomes a derivative,

$$\lim_{q_V \to 0}\left(\frac{q_V}{\Delta T}\right)_V \equiv \left(\frac{\partial q}{\partial T}\right)_V = C_V \quad . \qquad (1)$$

We have given this derivative the symbol, $C_V$, and we call it the "heat capacity at constant volume. Usually one quotes the "molar heat capacity,"

$$\overline{C}_V \equiv C_{Vm} = \frac{C_V}{n} \quad . \qquad (2)$$

We can rearrange Equation 1 as follows,

$$dq_V = C_V\, dT \quad . \qquad (3)$$

Then we can integrate this equation to find the heat involved in a finite change at constant volume,

$$q_V = \int_{T_1}^{T_2} C_V\, dT \qquad (4)$$

If $C_V$ is approximately constant over the temperature range then $C_V$ comes out of the integral and the heat at constant volume becomes,

$$q_V = C_V(T_2 - T_1) \quad . \qquad (5)$$

Let us now go through the same sequence of steps except holding pressure constant instead of volume. Our initial definition of the heat capacity at constant pressure, $C_p$ becomes,

$$\lim_{q_p \to 0}\left(\frac{q_p}{\Delta T}\right)_p \equiv \left(\frac{\partial q}{\partial T}\right)_p = C_p \quad . \qquad (6)$$

The analogous molar heat capacity is,

$$\overline{C}_p \equiv C_{pm} = \frac{C_p}{n} . \qquad (7)$$

Equation (6) rearranges to,

$$dq_p = C_p dT , \qquad (8)$$

which integrates to give,

$$q_p = \int_{T_1}^{T_2} C_p dT . \qquad (9)$$

When $C_p$ is approximately constant the integral in Equation (9) becomes

$$q_p = C_p(T_2 - T_1) . \qquad (10)$$

Very frequently the temperature range is large enough that $C_p$ cannot be regarded as constant. In these cases the heat capacity is fit to a polynomial (or similar function) in T. For example, some tables give the heat capacity as,

$$\overline{C}_p = \alpha + \beta T + \gamma T^2 , \qquad (11)$$

where $\alpha$ , $\beta$ , and $\gamma$ are constants given in the table. With this temperature-dependent heat capacity the heat at constant pressure would integrate as follows,

$$\begin{aligned} q_p &= n\int_{T_1}^{T_2} (\alpha + \beta T + \gamma T^2) dT \\ &= n\,\alpha(T_2 - T_1) + n\frac{\beta}{2}(T_2^2 - T_2^2) + n\frac{\gamma}{3}(T_2^3 - T_1^3) . \end{aligned} \qquad (12a, b)$$

Occasionally one finds a different form for the temperature dependent heat capacity in the literature,

$$\overline{C}_p = a + bT + cT^{-2} . \qquad (13)$$

When you do calculations with temperature dependent heat capacities you must check to see which form is being used for $C_p$.

1. We are using the convention that *q* will always designate **heat absorbed by** the system. *q* can be positive or negative and the sign indicates which way heat is flowing. If *q* is positive then heat was indeed absorbed by the system. On the other hand, if *q* is negative it means that the system gave up heat to the surroundings.

## Energy, the First Law, and Enthalpy

We have agreed that work, potential energy, kinetic energy, and heat are all forms of energy. Historically, it was not obvious that heat belonged in this list. But beginning with the experiments of Count Rumford of the Holy Roman Empire, and later the experiments of Joule, it became clear that heat, too, was just another form (or manifestation) of energy.

Recall that we defined the internal energy, *U*, as the total energy of the system. (Although the existence of atoms and molecules is not relevant to thermodynamics, we said that the internal energy is the sum of all the kinetic and potential energies of all the particles in the system. This statement is outside the realm of thermodynamics, but it is useful for us to gain an intuitive "feel" for what the internal energy is.)

Recall also that energies are always measured relative to some origin of energy. The origin is irrelevent to thermodynamics because we will always calculate changes in *U* and not absolute values of *U*. That is, we calculate

$$\Delta U \equiv U_{\text{final}} - U_{\text{initial}} . \qquad (1)$$

In words, this equation reads, "the change in the internal energy is equal to the final internal energy minus the initial internal energy." This equation also reminds us that *U* is a "state function." That is, the change in *U* does not depend on how the change was done (in other words, on the path), but depends only on the initial and final states.

Recall that the first law of thermodynamics in equation form for a finite change, is given by,

$$\Delta U = q + w . \qquad (2)$$

Equation (2) tells something else of importance. We know that *U* is a state function and that Δ*U* is independent of path. However, *w* is not a state function so that *w* depends on path. Yet the sum of *w* and *q* is path independent. The only way this can happen is if *q* is also path dependent. We now see that we are dealing with two path-dependent quantities, *q* and *w*.

For a differential change we write the first law in differential form,

$$dU = dq + dw . \qquad (3)$$

The *w* in Equation (2) or the *dw* in Equation (3)3 includes all types of work, work done in expansion and contraction, electrical work, work done in creating new surface area, and so on. Much of the work that we deal with in thermodynamics will be work done in expansion and contraction of the system, or *pV* work. Recall that the expression for *pV* work is,

$$dw = -pdV . \qquad (4)$$

If we want to include both *pV* work and other types of work we can write the first law as,

$$dU = dq - pdV + dw_{other} . \qquad (5)$$

Let's now confine ourselves to systems where there is only *pV* work. In this case the first law can be written,

$$dU = dq - pdV . \qquad (6)$$

Suppose we now regard *U* as a function of *T* and *V*. That is, *U* = *U*(*T,V*). Then, for *dU* we can write,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad . \qquad (7)$$

For a process at constant $V$ ($dV = 0$) Equations (6) and (7) become,

$$dU_V = dq_V \qquad (8)$$

and

$$dU_V = \left(\frac{\partial U}{\partial T}\right)_V dT \quad . \qquad (9)$$

We know, from our discussion on heat and heat capacity , that the differential heat at constant volume can also be written as,

$$dq_V = C_V dT \qquad (10)$$

so,

$$dU_V = C_V dT \quad . \qquad (11)$$

Comparing Equations (9) and (11), and recognizing that the change $dU_V$ is the same in both cases, we see that,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad . \qquad (12)$$

We shall regard Equation (12) as the formal thermodynamic definition of the heat capacity at constant volume. This new definition is more satisfactory than our previous temporary definition,

$$C_V = \left(\frac{\partial q}{\partial T}\right)_V \quad . \qquad (13)$$

Equation (12) is a better definition of the heat capacity because it is usually more satisfactory to define thermodynamics quantities in terms of state functions, like $U$, $T$, $V$, $p$, and so on, rather than on things like $q$ and $w$ which depend on path.

One other comment, we can integrate Equation (8), at constant volume, to get,

$$\Delta U_V = q_V \quad . \qquad (14)$$

In words, for any process at constant volume the heat, $q$, is the same as the change in the internal energy, $\Delta U$.

## Enthalpy

It turns out that $V$ is not the most convenient variable to work with or to hold constant. It is much easier to control the pressure, $p$, on a system than it is to control the volume of the system, especially if the system is a solid or a liquid. What we need is a new function, with units of energy, which contains all the information that is contained in $U$ but which can be controlled by controlling the pressure. Such a function can be defined (created) by a Legendre transformation. There are particular criteria which must be met in making a Legendre transformation, but in our case here these criteria are met. (A full discussion of the mathematical properties of Legendre transformations is beyond the scope of this discussion. There are more details given in the

Appendices to Alberty and Silby.) In our case we will define a new quantity, *H*, called the **enthalpy**, which has units of energy, as follows,

$$H = U + pV \quad . \qquad (15)$$

We can show that *H* is a natural function of *p* (in the same sense that *U* is a natural function of *V*) as follows,

$$\begin{aligned} dH &= dU + pdV + Vdp \\ &= dq - pdV + pdV + Vpd \\ &= dq + Vdp \end{aligned} \quad . \qquad (16a, b, c)$$

One of the great utilities of the enthalpy is that it allows us to use a state function, *H*, to describe the heat involved in processes at constant pressure rather than the heat, *q*, which is not a state function. To see this, let's go through the same process with *dH* that we did with *dU* above. Let's regard *H* as a function of *T* and *p* (for now). Then we can write,

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \quad . \qquad (17)$$

Consider a process at constant pressure (*dp* = 0). From Equation (16c) we conclude that.

$$dH_p = dq_p \qquad (18)$$

and from Equation (17) we get,

$$dH_p = \left(\frac{\partial H}{\partial T}\right)_p dT \quad . \qquad (19)$$

We know, from our discussion on heat and heat capacity , that the differential heat at constant pressure can also be written as,

$$dq_p = C_p dT \qquad (20)$$

so,

$$dH_p = C_p dT \quad . \qquad (21)$$

Comparing Equations (19) and (21), and recognizing that the change $dH_p$ is the same in both cases, we see that,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p . \qquad (22)$$

We shall regard Equation (22) as the formal thermodynamic definition of the heat capacity at constant pressure. Again, this definition is much more satisfactory than our previous temporary definition,

$$C_p = \left(\frac{\partial q}{\partial T}\right)_p , \qquad (23)$$

since it defines the heat capacity in terms of the state function, *H*, rather than in terms of *q* which is not a state function.

Just as we integrated equation (8), we can integrate Equation (21), at constant pressure, to get,

$$\Delta H_p = q_p . \qquad (24)$$

In words, for any process at constant pressure the heat, $q$, is the same as the change in enthalpy, $\Delta H$. This equation contains no approximations. It is valid for **all** process at constant pressure. Equation (24) is vastly more useful than its counterpart at constant volume because we carry out our chemistry at constant pressure much more often than we do at constant volume.

People sometimes ask, "What is the meaning of $H$?" Unfortunately, there is no simple, intuitive physical description of enthalpy like there is for the internal energy. (Recall that the internal energy is the sum of all kinetic and potential energies of all the particles in the system). The nearest thing we can come to as a description of $H$ is the one above where $\Delta H$ is the heat (gain or loss) in a constant pressure process. For this reason the enthalpy is ocassionally referred to as the "heat content."

Reminder: Nuclear energy was unknown to the original formulators of thermodynamics. We now know that matter can be converted into energy and vice versa. The "energy equivalent of matter" is given by the famous Einstein formula, $E = mc^2$, where $m$ is the mass of the matter and $c$ is the velocity of light. Since the velocity of light is very large, about $3 \times 10^8$ m/s, a small amount of mass is equivalent to a very large amount of energy. Strictly speaking, the statement, "energy is conserved," should be replaced by the statement, "energy plus the energy equivalent of mass is conserved." That is, energy + $mc^2$ is conserved. The conversion of mass to energy or energy to mass in chemical reactions is so small that it is virtually never observed in chemical problems. So, for chemical thermodynamics, the simpler statement that energy is conserved is sufficient.

## The Joule Expansion

Much of the early progress in thermodynamics was made in the study of the properties of gases. One of the early questions was whether or not gases cool on expansion. (Our intuition might tell us that they would, but is our intuition correct?)

Joule designed an experiment to find out whether or not gases cool on expansion and if so how much.

The Joule apparatus consisted of two glass bulbs connected by a stopcock. One bulb was filled with gas at some $p$ and $T$. The other bulb was evacuated. The entire apparatus was insulated so that $q = 0$. That is, the experiment would be adiabatic.

The stopcock was opened to allow the gas to expand into the adjoining bulb. Since the gas was expanding against zero pressure no work was done, $w = 0$. With both $q = 0$ and $w = 0$ it is clear that,

$$\Delta U = q + w = 0.$$

The process is at constant internal energy.

Clearly, $\Delta V \neq 0$ because the gas expanded to fill both bulbs. The question was, did $T$ change? $\Delta T$ was measured to be zero, no temperature change.

(It turns out that the Joule experiment was sufficiently crude that it could not detect the difference between an ideal gas and a real gas so that the conclusions we will draw from this experiments only apply to an ideal gas.)

In effect, Joule was trying to measure the derivative,

$$\left(\frac{\partial T}{\partial V}\right)_U,$$

and the result was that,

$$\left(\frac{\partial T}{\partial V}\right)_U = 0. \qquad (1)$$

This particular derivative is not all that instructive, with *U* being held constant. We can use our version of Euler's chain relation to obtain information that is more instructive.

$$\begin{aligned}\left(\frac{\partial T}{\partial V}\right)_U &= -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V} \\ &= \frac{\left(\frac{\partial U}{\partial V}\right)_T}{C_V} \\ &= 0. \end{aligned} \qquad (2a,\ b,\ c)$$

We know that $C_V$ for gases is neither zero nor infinity, so we must conclude that,

$$\left(\frac{\partial U}{\partial V}\right)_T = 0. \qquad (3)$$

This is an important and useful result. It says that the internal energy of an ideal gas is not a function of *T* and *V*, but of *T* only. That is, in equation form,

for an ideal gas $U = U(T)$. (4)

For real gases, and most approximations to real gases, like the van der Waals equation of state,

$$\left(\frac{\partial U}{\partial V}\right)_T \neq 0.$$

However, this quantity is quite small, even for real gases. We will have occasion to calculate it for the van der Waals equation of state later on.

This result extends to the enthalpy of an ideal gas.

$$H = U + pV = U(T) + nRT = H(T). \qquad (5)$$

Thus, for an ideal gas both *U* and *H* are functions of *T* only.

Then all of the following derivatives are zero:

$$\left(\frac{\partial U}{\partial V}\right)_T = 0,$$
$$\left(\frac{\partial U}{\partial p}\right)_T = 0,$$
$$\left(\frac{\partial H}{\partial V}\right)_T = 0,$$
$$\left(\frac{\partial H}{\partial p}\right)_T = 0. \qquad \text{(6a, b, c, d)}$$

We will now use some of these results to discuss that adiabatic expansion of an ideal gas.

## Adiabatic Expansion of an Ideal Gas

The definition of an adiabatic expansion, for now, is $dq = 0$. That is, no heat goes in or out of the system. However, $dw \neq 0$. As the gas expands it does work on the surroundings. Since the gas is cut off from any heat bath it cannot draw heat from any source to convert into work. The work must come from the internal energy of the gas so that the internal energy decreases. Since the internal energy of an ideal gas in only dependent on $T$ that means that the temperature of the gas must decrease.

From the first law with only $pV$ work we have

$$\begin{aligned} dU &= dq - pdV \\ &= -pdV \end{aligned} \qquad \text{(7a, b)}$$

because $dq = 0$ for an adiabatic process.

Regarding $U$ as a function of $T$ and $V$. That is, $U = U(T,V)$, we get

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ &= C_V dT, \end{aligned} \qquad \text{(8a, b)}$$

because of the definition of $C_V$ and because our gas is an ideal gas so that the second derivative vanishes (Equation (6a)) .

The $dU$ 's in Equations (7) and (8) must be equal so that

$$-pdV = C_V dT$$
$$-\frac{nRT}{V}dV = C_V dT. \qquad \text{(9a, b)}$$

Rearranging Equation (9b) we get

$$\frac{dT}{T} = -\frac{nR}{C_V}\frac{dV}{V}. \qquad (10)$$

By the same token, using enthalpy, we find

$$\begin{aligned} dH &= dq + Vdp \\ &= Vdp, \end{aligned} \qquad (11a, b)$$

and

$$\begin{aligned} dH &= \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \\ &= C_p dT, \end{aligned} \qquad (12a, b)$$

From which we deduce that

$$\frac{dT}{T} = \frac{nR}{C_p}\frac{dp}{p}. \qquad (13)$$

Comparing Equations (10) and (13) we see that

$$\begin{aligned} -\frac{nR}{C_V}\frac{dV}{V} &= \frac{nR}{C_p}\frac{dp}{p}, \\ -\frac{C_p}{C_V}\frac{dV}{V} &= \frac{dp}{p} \\ -\gamma\frac{dV}{V} &= \frac{dp}{p}, \end{aligned} \qquad (14a, b, c)$$

Where we have written $C_p/C_V = \gamma$ .

If we regard $C_p$ and $C_V$ as constant then Equation (14c) can be integrated to give,

$$\begin{aligned} -\gamma \ln\frac{V_2}{V_1} &= \ln\frac{p_2}{p_1}, \\ \gamma \ln\frac{V_1}{V_2} &= \ln\frac{p_2}{p_1}, \\ \ln\left(\frac{V_1^\gamma}{V_2^\gamma}\right) &= \ln\frac{p_2}{p_1}; \\ \frac{V_1^\gamma}{V_2^\gamma} &= \frac{p_2}{p_1}, \\ p_1V_1^\gamma &= p_2V_2^\gamma. \end{aligned} \qquad (15a, b, c, d, e)$$

Equation (15e) is the equation for the adiabatic expansion of an ideal gas. You have probably seen it before.

**Adiabatic Work - Ideal Gas**

We can use Equation (15e) as the equation for an adiabatic path on a $pV$ diagram.

$$\begin{aligned} pV^{\gamma} &= p_1 V_1^{\gamma} \\ p &= \frac{p_1 V_1^{\gamma}}{V^{\gamma}} \\ p &= \frac{\text{constant}}{V^{\gamma}}, \end{aligned}$$

(16a, b, c)

where $p_1$ and $V_1$ refer to some arbitrary constant point on the path. Equation (16b) gives $p$ as a function of $V$ along the adiabatic line. We have added Equation (16c) just to emphasize the point that $p_1$ and $V_1$ refer to some fixed (constant) point on the adiabatic expansion curve. With this expression for $p$ the work can be easily calculated,

$$\begin{aligned} dw &= -p\,dV \\ w &= -\int_{V_1}^{V_2} p\,dV \\ &= -\int_{V_1}^{V_2} \frac{\text{constant}}{V^{\gamma}}\,dV \\ w &= -\frac{\text{constant}}{-\gamma+1}\left(\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}}\right). \end{aligned}$$

(17a, b, c, d)

The constant is easily found from the knowledge of one point on the adiabatic line (path).

**The Joule-Thompson Expansion**

It soon became apparent that the result of the Joule expansion experiment was not valid for real gases. A more accurate experiment, slightly different, was carried out by Joule and J. J. Thompson to further elucidate the properties on real gases under expansion.

A sample of a gas, initially at $p_1$, $V_1$, and $T_1$ was forced through a porous plug at constant pressure, $p_1$. The gas came out of the other side of the plug at $p_2$, $V_2$, and $T_2$. The apparatus was insulated so that $q = 0$. The work has two terms, the work done on the system to force the gas through the plug and the work done by the system on the surroundings as it came out the other side of the plug.

The total work is

$$\begin{aligned} w &= -p_1(0 - V_1) - p_2(V_2 - 0) \\ &= p_1V_1 - p_2V_2. \end{aligned}$$

(18a, b)

Since $q = 0$, the change in internal energy of the gas is,

$$\begin{aligned} \Delta U &= q + w \\ &= 0 + p_1V_1 - p_2V_2 \\ &\neq 0. \end{aligned}$$

(19a, b, c)

This process, unlike the Joule expansion, is not at constant internal energy.

The enthalpy, however, is given by,

$$\begin{aligned} \Delta H &= \Delta U + \Delta(pV) \\ &= p_1V_1 - p_2V_2 + p_2V_2 - p_1V_1 \\ \Delta H &= 0. \end{aligned}$$

(20a, b, c)

So the Joule Thompson experiment is a process at constant enthalpy. In the experiment they could select a value for $\Delta p$, and then measure $\Delta T$. The ratio of these two quantities is an approximation to a derivative,

$$\frac{\Delta T}{\Delta p} \approx \left(\frac{\partial T}{\partial p}\right)_H = \mu_{\mathrm{JT}}.$$

(21)

$\mu_{\mathrm{JT}}$ is called the "coefficient of the Joule-Thompson effect." This coefficient is not zero for a real gas (or for realistic equations of state like the van der Waals equation of state), but we will now show that it *is* zero for an ideal gas. Applying the Euler chain rule to Equation (21) we obtain,

$$\begin{aligned} \left(\frac{\partial T}{\partial p}\right)_H &= -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} \\ &= -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{C_p}. \end{aligned}$$

(22a, b)

The numerator in Equation (22b) is zero for an ideal gas, but not necessarily zero for a real gas.

The coefficient of the Joule-Thompson effect is important in the liquefaction of gases because it tells whether a gas cools or heats on expansion. It turns out that this coefficient is a decreasing function of temperature and it passes through zero at the Joule-Thompson inversion temperature, $T_{\mathrm{I}}$. In an expansion $dp < 0$. Whether $dT$ is positive or negative depends on the sign of $\mu_{\mathrm{JT}}$. Looking at the definition of $\mu_{\mathrm{JT}}$,

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial p}\right)_H,$$

we see that if $\mu_{\mathrm{JT}}$ is positive then $dT$ is negative upon expansion so that the gas cools. On the other hand, if $\mu_{\mathrm{JT}}$ is negative, then $dT$ is positive so that the gas warms upon expansion. In order to liquefy a gas by a Joule-Thompson expansion the gas must first be cooled to below the J-T inversion temperature. Some inversion temperatures are:

| | |
|---|---|
| He | 40 K |
| $N_2$ | 621 K |
| $O_2$ | 764 K |
| Ne | 231 K |

We see that $N_2$ and $O_2$ will cool upon expansion at room temperature, but He and Ne will warm upon expansion at room temperature.

## The "Thermodynamic Equation of State"

We have seen that the results of the Joule expansion (valid for ideal gases) demonstrated experimentally that for an ideal gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = 0. \tag{1}$$

It would be advantageous to be able to calculate this quantity from an equation of state or other $pVT$ data. There is an equation which we will prove later, but which we introduce now because it is so useful, called the "thermodynamic equation of state, which will allow us to do this. It allows us to calculate the derivative in Equation (1) from an equation of state.

The equation is,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p. \tag{2}$$

This equation will be proved easily once we have the second law of thermodynamics. For now we will just accept it conditionally until it can be proved. Notice that the right- hand side contains nothing but $pVT$ data. We can see that the equation is at least plausible by checking that it does give zero for an ideal gas.

For an ideal gas,

$$p = \frac{nRT}{V}$$

so

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

Then,

$$\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial p}{\partial T}\right)_V - p \\ &= T\left(\frac{nR}{V}\right) - p \\ &= p - p \\ &= 0.\end{aligned}$$

We can also check to see what our thermodynamic equation of state would give for a van der Waals gas. For the van der Waals gas we find,

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2},$$

so

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

and

$$\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{nR}{V - nb}\right) - \left(\frac{nRT}{V - nb} - \frac{an^2}{V^2}\right) \\ &= +\frac{an^2}{V^2}.\end{aligned}$$

We know that $a$ is small and $n^2/V^2$ will be small except at very high pressures (densities). (The above result can be understood based on what is going on in the gas. When a gas expands at constant temperature it absorbs heat from the surroundings and does work on the surroundings. If the gas is ideal the heat and work exactly balance so that there is no change in the internal energy of the gas. In a van der Waals gas - and real gases - the expansion must also overcome the intermolecular forces so part of the heat absorbed from the surroundings goes to overcoming the intermolecular forces. The $a$ term in the van der Waals equation of state accounts for intermolecular forces. If you calculate the work in expanding a van der Waals gas you will see that that the part of the work that is proportional to $a$ is positive so that this work was done on the system - it raised the internal energy of the system.)

In most cases

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

is still pretty small, even for a van der Waals gas.

There is a companion to Equation (2),

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p . \qquad (3)$$

This equation can be derived (without the second law) from Equation (2) so that if Equation (2) is correct, so is Equation (3).

We will leave it to the reader to show that Equation (3) gives zero for an ideal gas. Applying this equation to the van der Waals gas is a little more involved and not particularly enlightening.

**Relationship Between $C_p$ and $C_V$**

$C_p$ and $C_V$ are related to each other and their difference can be calculated from an equation of state. We wish to prove that

$$C_p = C_V + T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p . \qquad (8d)$$

Let's begin with the definitions of $C_p$ and $H$,

$$\begin{aligned} C_p &= \left(\frac{\partial H}{\partial T}\right)_p \\ &= \left(\frac{\partial [U + pV]}{\partial T}\right)_p \\ &= \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p . \end{aligned} \qquad (4a, b, c)$$

The second term in (4c) is in an acceptable form, but the first term is not. (The wrong variable is being held constant.) To deal with the first term regard $U$ as $U = U(T,V)$. Then,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV. \qquad (5)$$

Now divide Equation (5) by $dT$ and hold $p$ constant. (Your calculus teacher won't like this, but you can prove that the result is correct and that this procedure will always work.) We obtain,

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p . \qquad (6)$$

Now we substitute Equation (6) for the appropriate term in Equation (4c) to get,

$$C_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$
$$= \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p . \qquad (7,a\ b)$$

But

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p. \qquad (2)$$

Substituting Equation (2) in for $(\partial U/\partial T)_V$ in Equation (7b) gives

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$
$$= \left(\frac{\partial U}{\partial T}\right)_V + \left(T\left(\frac{\partial p}{\partial T}\right)_V - p\right)\left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$
$$= C_V + T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$
$$= C_V + T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p , \qquad (8a, b, c, d)$$

Which is the desired result. We will let the reader show, using Euler's chain relation and the definitions of $\alpha$ and $\kappa$ , that this relation can be rewritten as

$$C_p = C_V + TV\frac{\alpha^2}{\kappa}. \qquad (9)$$

The second term on the right of Equation (9) is necessarily positive because $\kappa$ is always positive. $\alpha$ can be negative (water near 0$^o$C), but it appears here as the square. Thus $C_p > C_V$. For solids and liquids the second term on the right of Equation (9) is usually small. For gases it can be large. For an ideal gas we found earlier that $\alpha = 1/T$ and $\kappa = 1/p$ so that

$$C_p = C_V + nR.$$

## Thermochemistry

Thermochemistry is the subject that deals with the heats involved in chemical reactions. A typical chemical reaction might have a form similar to the following hypothetical chemical reaction:

$a$ A + $b$ B → $c$ C + $d$ D. (1)

(In Equation (1) the upper case letters stand for elements or compounds and the lower case letters stand for small whole numbers which balance the reaction. You would read this as saying, "*a* moles of A reacts with *b* moles of B to give *c* moles of C and *d* moles of D.")

A chemical reaction is a process just like any other thermodynamic process. It has an initial state (the reactants) and a final state (the products). We can calculate the changes in internal energy, enthalpy, and so on for the reaction. For example,

$\Delta U = U_{\text{products}} - U_{\text{reactants}}$
and
$\Delta H = H_{\text{products}} - H_{\text{reactants}}$.
One thing is sometimes not made very clear. "Reactants" and "products" in these equations means that the reactants and products are separated, isolated, and pure. Furthermore, the reactants and products are all at the same temperature and pressure. So, for example, the $\Delta H$ above is the enthalpy of $c$ moles of C (isolated and pure in its own container at temperature, $T$, and pressure, $p$) plus the enthalpy of $d$ moles of D (isolated and pure in its own container at temperature, $T$, and pressure, $p$) minus the enthalpy of $a$ moles of A (isolated and pure in its own container at temperature, $T$, and pressure, $p$) minus the enthalpy of $b$ moles of B (isolated and pure in its own container at temperature, $T$, and pressure, $p$).

From time to time we will add a superscript $^{\text{o}}$ to $H$ or $U$ to indicate that reactants and products are in their "standard states." That is, they are in their most stable state at $T$ and $p$. For example, the standard state of water at 25$^{\text{o}}$C and 1 atm pressure is liquid water.

If our reaction takes place at constant $V$, as in a bomb calorimeter, $dV = 0$ and

$\Delta U_V = q_V$.
If the reaction takes place at constant $p$, as in open to atmospheric pressure, $dp = 0$ and
$\Delta H_p = q_p$.
If $\Delta H_p < 0$ we say that the reaction is exothermic. That is, the system gave heat to the surroundings. On the other hand, if $\Delta H_p > 0$ we say that the reaction is endothermic. The system absorbed heat from the surroundings.

From the definition of enthalpy we find that

$\Delta H = \Delta U + \Delta(pV)$, (2)
where
$\Delta(pV) = (pV)_{\text{products}} - (pV)_{\text{reactants}}$.
For liquids and solids $\Delta(pV)$ is quite small. $\Delta(pV)$ is not necessarily small for gases, but we can get a reasonable estimate for this quantity by approximating the gases as ideal. Then
$\Delta(pV)_{\text{gas}} \approx (pV)_{\text{gas products}} - (pV)_{\text{gas reactants}} \approx n_{\text{gas products}} RT - n_{\text{gas reactants}} RT = RT\Delta n_{\text{gas}}$,
where $\Delta n_{\text{gas}}$ is the difference in the number of moles of gaseous products and reactants. Using this approximation we get
$\Delta H = \Delta U + RT\Delta n_{\text{gas}}$. (3)
However, we have to be careful how we understand this equation because the conditions of the reaction must be the same on both sides of the equation. Since $\Delta H$ is the heat we measure if the reaction is run and constant pressure ($\Delta H_p = q_p$) and $\Delta U$ is the heat we measure if the reaction is run at constant volume ($\Delta U_V = q_V$), it is tempting (and common) to write Equation (3) as
$q_p = q_V + RT\Delta n_{\text{gas}}$. (4)

However, Equation (4) cannot be rigorously true since the $q$'s refer to different conditions, one at constant $p$ and one at constant $V$. We can get an indication whether or not Equation (4) is a good approximation with the following example:

Consider the reaction.

$2\,C(s) + O_2(g) \rightarrow 2\,CO(g)$, (5)
run at $dV = 0$.
$\Delta\,(pV) \approx \Delta\,(pV)_{gas} \approx RT\Delta\, n_{\,gas} = RT$.
The heat measured is $q_V$. Now let us find a way to measure $q_p$ Consider the following two steps

$$\begin{array}{ccccc} 2\,C(s) + O_2(g) & \rightarrow & 2\,CO(g) & \rightarrow & 2\,CO(g) \\ p_1, V_1, T, & q_V & p_2, V_1, T, & \Delta H_2 & p_1, V_2, T. \end{array} \qquad (6)$$

The first step is the constant volume reaction we had before with $\Delta U_V = q_V$. Notice that the pressure increases. The second step takes the product of the constant volume reaction and reduces the pressure back to the original pressure. We call the heat for this step $\Delta H_2$. So it is rigorously true that

$$\Delta H_p = \Delta H_V + \Delta H_2 = q_V + RT + \Delta H_2. \qquad (7)$$

However, the $\Delta H_2$ term is the enthalpy for the expansion of a gas at constant temperature. If the gas is ideal this term is zero. For real gases this term would be very small, so we make a negligible error is neglecting it. So to pretty good approximation we can use the equation,

$$q_p = q_V + RT\Delta\, n_{\,gas}. \qquad (4)$$

## Hess' Law

Hess' law states that if you add or subtract chemical reaction equations you can (must) add or subtract their corresponding $\Delta H$'s or $\Delta U$'s to get $\Delta H$ or $\Delta U$ for the overall reaction. For example, if we add the reaction

$a\,A + b\,B \rightarrow c\,C + d\,D.$ $\Delta H_1, \Delta U_1$
to the reaction
$e\,E + f\,F \rightarrow g\,G + h\,H$ $\Delta H_2, \Delta U_2$
to get
$a\,A + b\,B + e\,E + f\,F \rightarrow c\,C + d\,D + g\,G + h\,H$,
Then, for the overall reaction
$\Delta H = \Delta H_1 + \Delta H_2$ and $\Delta U = \Delta U_1 + \Delta U_2$.
The great utility of Hess' law is that we don't have to tabulate $\Delta H$ for every possible reaction. We can get $\Delta H$ for a particular reaction by adding and subtracting $\Delta H$'s for a much smaller set of reactions, called formation reactions. We define $\Delta_f H^{o}$ for a compound to be the enthalpy of the reaction:

pure, isolated elements, in their standard (most stable) states
→ one mole of compound in its standard state.

For example, the heat of formation of liquid water is defined as $\Delta H^{\circ}$ for the reaction,

$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$.
By definition, then, the heat of formation for an element in its most stable state is zero.

To obtain $\Delta H^{\circ}$ for the hypothetical reaction, Equation (1), we add and subtract the appropriate heats of formations,

$$\Delta_r H^{\circ} = c\Delta_f H_C^{\circ} + d\ \Delta_f H_D^{\circ} - a\ \Delta_f H_A^{\circ} - b\ \Delta_f H_B^{\circ}. \qquad (8)$$

For example, $\Delta H^{\circ}$ for the reaction,
$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$, (9)
is given by

$$\begin{aligned}\Delta_r H^{\circ} &= \Delta_f H^{\circ}_{CO_2(g)} + 2\Delta_f H^{\circ}_{H_2O(l)} - \Delta_f H^{\circ}_{CH_4(g)}\\ &= 1\ \text{mol} \times (-393.51\frac{\text{kJ}}{\text{mol}}) + 2\ \text{mol} \times (-285.83\frac{\text{kJ}}{\text{mol}}) - 1\ \text{mol} \times (-74.81\frac{\text{kJ}}{\text{mol}})\\ &= -890.36\ \text{kJ}.\end{aligned}$$

(We don't always write out explicitly that the coefficients which balance the reaction have units, but we have done so here to make it clear that these numbers have units. This will become an issue later.)

## $\Delta H$ at Other Temperatures

Tables of heats of formation usually give data for reactions at 25°C. We frequently need to know the heat of a reaction at a temperature other than 25°C. If we know the heat capacities at constant pressure we can calculate the heat of reaction at a temperature other than 25°C. We use the following chain of reasoning. We know that,

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

then

$$\left(\frac{\partial H^{\circ}}{\partial T}\right)_p = C_p^{\circ}$$

and

$$\left(\frac{\partial \Delta H^{\circ}}{\partial T}\right)_p = \Delta C_p^{\circ}, \qquad (10a, b, c)$$

where $\Delta C_p^{\circ}$ is defined for our hypothetical chemical reaction, Equation (1) as,

$$\Delta C_p^{\circ} = c\ C_{pC}^{\circ} + d\ C_{pD}^{\circ} - a\ C_{pA}^{\circ} - b\ C_{pB}^{\circ}. \qquad (11)$$

Prepare Equation 10c for integration as

$$d\Delta H^\circ = \Delta C_p^\circ \, dT, \tag{12}$$

and integrate,

$$\Delta H^\circ(T_2) = \Delta H^\circ(T_1) + \int_{T_1}^{T_2} \Delta C_p^\circ dT. \tag{13}$$

For very accurate work we will have to use the temperature dependent heat capacities in Equations (11) and (13), but more often than not we can regard the heat capacities as approximately constant over the temperature range, so that Equation (13) becomes,

$$\Delta H^\circ(T_2) = \Delta H^\circ(T_1) + \Delta C_p^\circ(T_2 - T_1). \tag{14}$$

As an example, let's calculate the heat of reaction for the reaction in Equation (9) at 95°C.

$\Delta C_p^{\mathrm{o}}$ for the reaction in Equation (9) is given by,

$$\begin{aligned}\Delta_r C_p^\circ &= C^\circ_{p\mathrm{CO_2}(g)} + 2C^\circ_{p\mathrm{H_2O}(l)} - C^\circ_{p\mathrm{CH_4}(g)} - 2C^\circ_{p\mathrm{O_2}(g)} \\ &= 1\,\mathrm{mol} \times (37.11\frac{\mathrm{J}}{\mathrm{K\,mol}}) + 2\,\mathrm{mol} \times (75.291\frac{\mathrm{J}}{\mathrm{K\,mol}}) \\ &\quad -1\,\mathrm{mol} \times (35.31\frac{\mathrm{J}}{\mathrm{K\,mol}}) - 2\,\mathrm{mol} \times (29.355\frac{\mathrm{J}}{\mathrm{K\,mol}}) \\ &= 93.67\,\frac{\mathrm{J}}{\mathrm{K}}.\end{aligned} \tag{15}$$

Then, Equation (14) gives,

$$\begin{aligned}\Delta H^\circ(95\,^\circ\mathrm{C}) &= \Delta H^\circ(25\,^\circ\mathrm{C}) + \Delta C_p^\circ(368.15 - 298.15) \\ &= -890.36\,\mathrm{kJ} + 93.67\,\frac{\mathrm{J}}{\mathrm{K}} \times 70\,\mathrm{K}\,\frac{1\,\mathrm{kJ}}{1000\,\mathrm{J}} \\ &= -\,883.80\,\mathrm{kJ}\end{aligned} \tag{16}$$

(Note: There is another way to do this problem. Calculate $\Delta H^{\mathrm{o}}$ for cooling the reactants down to 25°C, calculate $\Delta H^{\mathrm{o}}$ for the reaction at 25°C, calculate $\Delta H^{\mathrm{o}}$ for heating the products back up to 95°C, and then add them up. Since $H$ is a state function $\Delta H$ is independent of path. This method will also work if one of the components of the reaction has a phase change somewhere in the temperature range.

For example, if we let the new temperature be over 100°C we would have to account for the vaporization of the liquid water product. This is not hard to do, but requires some extra steps, including also the use of the heat capacity of water vapor. If the upper temperature in this problem is above 100°C we carry out the reaction in several steps:

Step 1 - Cool the reactants from the upper temperature to 25°C,
Step 2 - Run the reaction at 25°C,
Step 3 - Heat the product $CO_2$ from 25°C to the upper temperature,
Step 4 - Heat the liquid water from 25°C to 100°C,

Step 5 - Vaporize the water at 100°C,
Step 6 - Heat the water vapor from 100°C to the upper temperature.
The heat of reaction at the upper temperature is the sum of the $\Delta H$'s for all six steps. Again we have taken advantage of the fact that $\Delta H$ is independent of path.)

## ***Δ H*** **as Making and Breaking Chemical Bonds**

Breaking a chemical bond is an endothermic process. That is, you must put energy into the system to break the bond.

Forming a chemical bond is an exothermic process. The energy released in forming the bond goes into the surroundings.

We can make an estimate of the $\Delta H$ for a chemical reaction by adding the bond energies of all the bonds broken and subtracting the bond energies of all the bonds formed.

$\Delta H \approx \mathrm{BE}_{\text{bonds broken}} - \mathrm{BE}_{\text{bonds formed}}$.
Let's try it on the gas phase reaction,
$N_2 + 3\ H_2 \rightarrow 2\ NH_3$.
(There are tables of bond energies in physical chemistry texts and in data handbooks. From the tables we find the following bond energies:

| | |
|---|---|
| N−N | 945 kJ |
| H−H | 436 kJ |
| N−H | 388 kJ. |

In the reaction we break 1 N−N bond and 3 H−H bonds. We form 6 N− H bonds. The approximate $\Delta H$ is then,
$\Delta H \approx 1 \times 945 + 3 \times 436 - 6 \times 388 = -75$ kJ.
This can be compared to the actual value of − 92 kJ. The method is not super accurate, but it gives a ball-park answer and might be useful in cases where other data are not available. Further, however it demonstrates graphically that the heat of a reaction is related to the making and breaking of chemical bonds.

## **Heats of Formation of Ions in Water Solution**

When you look in a table of heats of formation you find values listed for ions in water solutions. That is, you will find an entry for species such as $Na^+(aq)$. It is fair to ask where these numbers come from. We know that in equilibrium chemistry it is impossible to prepare $Na^+(aq)$ ions in solution all by themselves. It is possible to prepare a solution that has both $Na^+(aq)$ and $Cl^-(aq)$ ions, but not a solution that has only ions of one charge.

The heats of formation of solutions of soluble ionic compounds can be measured. That is, we can measure the heat of formation of HCl(*aq*). The heat of formation of HCl(*aq*) is defined as $\Delta H^{\mathrm{o}}$ for the reaction,

$1/2\ H_2(g) + 1/2\ Cl_2(g) \rightarrow HCl(aq)$. (17)

Since ionic compounds in solution are completely dissociated, it must be true that

$$\Delta_f H^\circ_{\mathrm{HCl}(aq)} = \Delta_f H^\circ_{\mathrm{H^+}(aq)} + \Delta_f H^\circ_{\mathrm{Cl^-}(aq)}. \tag{18}$$

We cannot know the heat of formation of either of the ions in solution, but we do know their sum.

By convention we arbitrarily set the heat of formation of the $H^+(aq)$ ion equal to zero. That is,

$$\Delta_f H^\circ_{\mathrm{H^+}(aq)} \equiv 0. \tag{19}$$

Then the heats of formation of all other aqueous ions can be determined relative to the heat of formation of the $H^+(aq)$ ion. As a start, we see that

$$\begin{aligned} \Delta_f H^\circ_{\mathrm{Cl^-}(aq)} &= \Delta_f H^\circ_{\mathrm{HCl}(aq)} - \Delta_f H^\circ_{\mathrm{H^+}(aq)} \\ &= \Delta_f H^\circ_{\mathrm{HCl}(aq)} - 0 \\ &= \Delta_f H^\circ_{\mathrm{HCl}(aq)} \end{aligned} \tag{20a, b, c}$$

This convention allows us to build up a table of heats of formation of aqueous ions.

For example, from the measured value of the heat of formation of NaCl(*aq*) and the knowledge that

$$\Delta_f H^\circ_{\mathrm{NaCl}(aq)} = \Delta_f H^\circ_{\mathrm{Na^+}(aq)} + \Delta_f H^\circ_{\mathrm{Cl^-}(aq)}. \tag{21}$$

we find that

$$\begin{aligned} \Delta_f H^\circ_{\mathrm{Na^+}(aq)} &= \Delta_f H^\circ_{\mathrm{NaCl}(aq)} - \Delta_f H^\circ_{\mathrm{Cl^-}(aq)} \\ &= \Delta_f H^\circ_{\mathrm{NaCl}(aq)} - \Delta_f H^\circ_{\mathrm{HCl}(aq)}. \end{aligned} \tag{22a, b}$$

Continuing these procedures we can define the heats of formations of other aqueous ions,

$$\begin{aligned} \Delta_f H^\circ_{\mathrm{Br^-}(aq)} &= \Delta_f H^\circ_{\mathrm{HBr}(aq)} - \Delta_f H^\circ_{\mathrm{H^+}(aq)} \\ &= \Delta_f H^\circ_{\mathrm{HBr}(aq)} - 0 \\ &= \Delta_f H^\circ_{\mathrm{HBr}(aq)}. \end{aligned} \tag{23a, b, c}$$

We now have enough data in our table to calculate the heat of formation of aqueous NaBr without measuring it.,

$$\begin{aligned} \Delta_f H^\circ_{\mathrm{NaBr}(aq)} &= \Delta_f H^\circ_{\mathrm{Na^+}(aq)} + \Delta_f H^\circ_{\mathrm{Br^-}(aq)} \\ &= \Delta_f H^\circ_{\mathrm{NaCl}(aq)} - \Delta_f H^\circ_{\mathrm{HCl}(aq)} + \Delta_f H^\circ_{\mathrm{HBr}(aq)}. \end{aligned} \tag{24a, b}$$

If the heat of formation of $H^+(aq)$ were set to some value other than zero, it would have cancelled out of Equation (24b). In this manner an entire table of heats of formation of aqueous ions can be built with all values relative to the heat of formation of the $H^+(aq)$ ion.

## Exact and Inexact Differentials

### A Mathematical Digression

We have mentioned, from time to time, that the quantities, $U$, $H$, and so on, are state functions, but that $q$ and $w$ are not state functions. This has various consequences. One consequence is that we can write things like $\Delta U$ and $\Delta H$, but we never write $q$ or $w$ with a $\Delta$ in front them. A more important consequence is that in a process $\Delta U$ and $\Delta H$ are independent of path. That is, $\Delta U$ and $\Delta H$ depend only on the initial and final states. However, $q$ and $w$ do depend on the path one takes to get from the initial to the final state.

Another consequence is that the differentials, $dU$ and $dH$ are mathematically different, in some sense, from $dq$ and $dw$. Some writers write $dq$ and $dw$ with a line through the $d$ to indicate this difference. We have not chosen to use such a specialized notation, but expect that we all will be able to just remember that $dU$ and $dH$ are mathematically different, in some sense, than $dq$ and $dw$.

We must now consider in detail the nature of this difference.

Let's think, for the moment, in terms of functions of the variables $x$ and $y$ and consider the differential,

$$df = 2xy^3dx + 3x^2y^2dy. \qquad (1)$$

We ask the question, does there exist a function, $f = f(x,y)$ such that,

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy. \qquad (2)$$

In other words, does a function $f(x,y)$ exist such that,

$$\left(\frac{\partial f}{\partial x}\right)_y = 2xy^3$$

and

$$\left(\frac{\partial f}{\partial y}\right)_x = 3x^2y^2 \,? \qquad (3a, b)$$

Euler's test provides a way to see whether such a function, $f(x,y)$ exists. Euler's test is based on the fact that for "nice" functions (and all of our functions are "nice") the mixed second derivatives must be equal. That is,

$$\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right). \qquad (4)$$

(On the left-hand side we take the derivative with respect to $y$ first and then take the derivative of the result with respect to $x$, and vice versa on the right-hand side.

Let's try Euler's test on our differential, $df$. If $f$ exists then the Equations (3a) and (3b) are correct. Use Equations (3a, b) to obtain the proposed second derivatives,

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y = \frac{\partial}{\partial y}2xy^3 = 6xy^2$$

and

$$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x = \frac{\partial}{\partial x}3x^2y^2 = 6xy^2. \qquad (5a, b)$$

The mixed second derivatives are equal. So we conclude that there exists a function, $f(x,y)$ (actually $x^2y^3$) such that Equations (1) and (2) are equal.

The differential $df$, in Equation (1), is called an "exact differential" for the very reason that a function, $f$, exists such that Equation (2) can be used to calculate it.

Now, let's consider the differential,

$$dg = 2x^2y^3dx + 3x^3y^2dy. \qquad (6)$$

Is $dg$ an exact differential? Use Euler's test to find out. If $dg$ is exact then the coefficients of $dx$ and $dy$ are the respective partial derivatives of $g$. Euler's test would then compare

$$\frac{\partial}{\partial y}2x^2y^3 = 6x^2y^2$$

with

$$\frac{\partial}{\partial x}3x^3y^2 = 9xy^2. \qquad (7)$$

These are not equal so that the putative second partial derivatives are not equal to each other. The differential, $dg$, is not exact and there does not exist a function, $g(x,y)$, such that $dg$ gives Equation (6).

Both of the differentials, $df$ and $dg$ can be integrated from, say, $x_1$, $y_1$ to $x_2$, $y_2$. The integral,

$$\int df = f(x_2,y_2) - f(x_1,y_1). \qquad (8)$$

depends only on the initial and final points because $df$ is exact and the function $f$ exists.

The differential $dg$ can be integrated, but there is no equivalent to Equation (8) for the integral of $dg$ because there is no function, $g(x,y)$ which gives Equation (6). The integral of $dg$ would have to be carried out along some path and we would find that the value of the integral depends on the path as well as on the initial and final points.

So, what is the purpose of all this? We are getting ready to present the second law of thermodynamics. One of the consequences of the second law will be the demonstration that for a reversible process $dq/T$ is exact. $dq_{\text{rev}}$ is not exact, but $dq_{\text{rev}}/T$ is exact. That means that $dq_{\text{rev}}/T$ is the differential of some new function (a state function) whose integral is independent of path. We will call the new state function, $S$, and name it the "entropy."

The absolute temperature, $T$, is called an "integrating denominator" for $dq_{\text{rev}}$. That is, when we divide the inexact differential, $dq_{\text{rev}}$, by $T$ the resulting differential becomes exact. Notice that the inexact differential, $dg$ above, has an integrating denominator. The variable, $x$, is an integrating denominator for $dg$. You can see this by noticing that $dg/x = df$.

## Second Law of Thermodynamics - Introduction

### Word Statements of Second Law

When we introduced the first law of thermodynamics we claimed that it is a statement of repeated observation elevated to the status of a law. No one has ever been able to make a machine that produces work out of nothing (a perpetual motion machine of the first kind), so we assume that no such machine can be made.

We then write this statement in mathematical language and begin deriving the consequences of the statement. Ultimately, the validation of the law comes from the experimental verification of the consequences.

The second law of thermodynamics is also a statement of repeated observation (or perhaps better yet, a statement of some things that have never been observed).

Here are two things that have never been observed:

1. Heat has never been observed to move spontaneously from a cold body to a hot body.
2. Heat has never been observed to be converted entirely into work with no other result.

So the second law, in words, is just the statement that these two things are impossible. that is:

1. It is impossible for heat to move spontaneously from a cold body to a hot body with no other result.
2. It is impossible to convert heat quantitatively into work with no other result.

The latter statement is sometimes phrased: "It is impossible to make a perpetual motion machine of the second kind."
(A perpetual motion machine of the second kind is a machine that converts heat into work without doing anything else. Imagine an ocean liner that scoops up liquid water out of the ocean, pulls the heat out of the water and uses it to power the ship, and dumps the left-over ice cubes out the back of the ship.

Note that a perpetual motion machine of the second kind would not violate the first law. Energy would be conserved because any heat extracted would be converted into work.)

The second law is why automobiles have radiators. Someone might ask why we throw away all that energy that dissipates from the radiator. Why not capture the energy and use it do decrease our gas mileage? The answer is that if you don't dissipate the heat the engine burns up, as you would quickly find out if you bypassed the radiator with a hose or if you drained the coolant from the radiator.

In order to convert these word statements into mathematical statements we can use we will have to develop some apparatus.

First we define the "heat engine." A heat engine is a cyclic process that absorbs heat from a heat bath and converts it into work. We shall see that in the cyclic process the engine also dissipates some heat to a heat bath at a lower temperature.

A crucial feature of the heat engine is that it returns to its original state after each cycle. That means that for each cycle of the engine itself, $\Delta H = 0$, $\Delta U = 0$, $\Delta T = 0$, and so on. Presumably, less heat is given back at the lower temperature than was absorbed at the upper temperature so that the difference can be used to supply work to the surroundings. (Otherwise we wouldn't have much of an engine.)

If you run the engine backwards by providing an external power source you get a heat pump (or a refrigerator), that is, a machine that absorbs heat from a lower temperature heat bath and gives it back to a heat bath at a higher temperature. But it takes work to do this.

Our procedure will be as follows:

1. Define and characterize a particular heat engine, the Carnot Cycle. The Carnot cycle is a heat engine operating between two heat baths, one at an upper temperature, which we shall call $T_U$ and the other at a lower temperature, $T_L$. The Carnot cycle uses the expansion and compression of an ideal gas to convert heat into work.

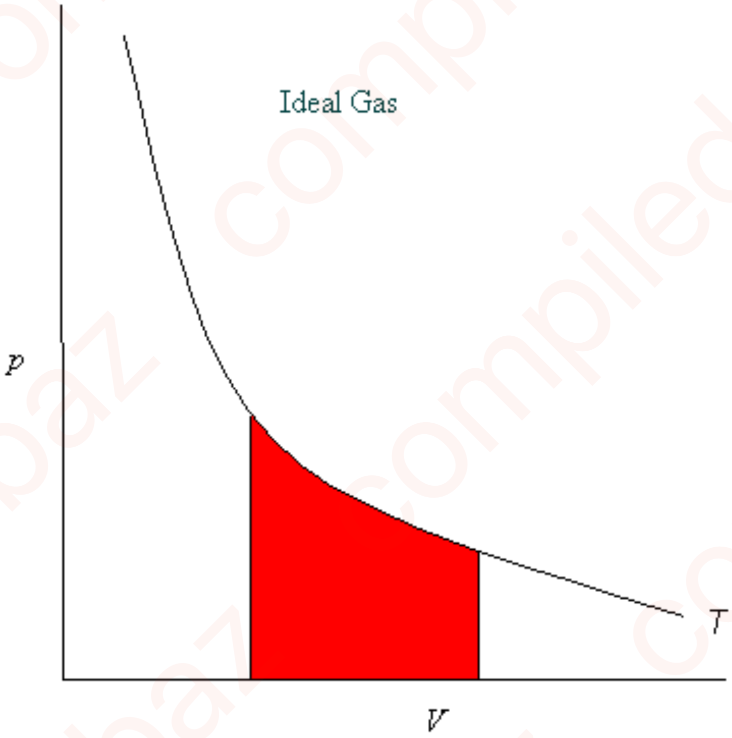
2. Define the efficiency, $e$, of a Carnot cycle.

3. Assume that we can find a heat engine, operating between the same two temperatures, which has efficiency greater than a Carnot cycle efficiency and then show that this violates both of the word statements of the second law given above. This leads to the conclusion that no heat engine or cycle can have an efficiency greater than the efficiency of a Carnot cycle.

4. The conclusion that no cycle can have an efficiency greater than a Carnot cycle will lead us to the further conclusion that the integral of $dq_{\text{rev}}/T$ is independent of path. Therefore, the differential $dq_{\text{rev}}/T$ must be exact, which means that it is the differential of some state function which we will call, $S$. That is, $dq_{\text{rev}}/T = dS$.

5. Another cycle can have an efficiency *less than* the efficiency of a Carnot cycle. This will lead us to the conclusion that $dq/T$ might be less than $dS$ if there is some irreversibility in the process. Putting the two possibilities together we will conclude that, $dq/T \leq dS$. This is the mathematical statement of the second law of thermodynamics.

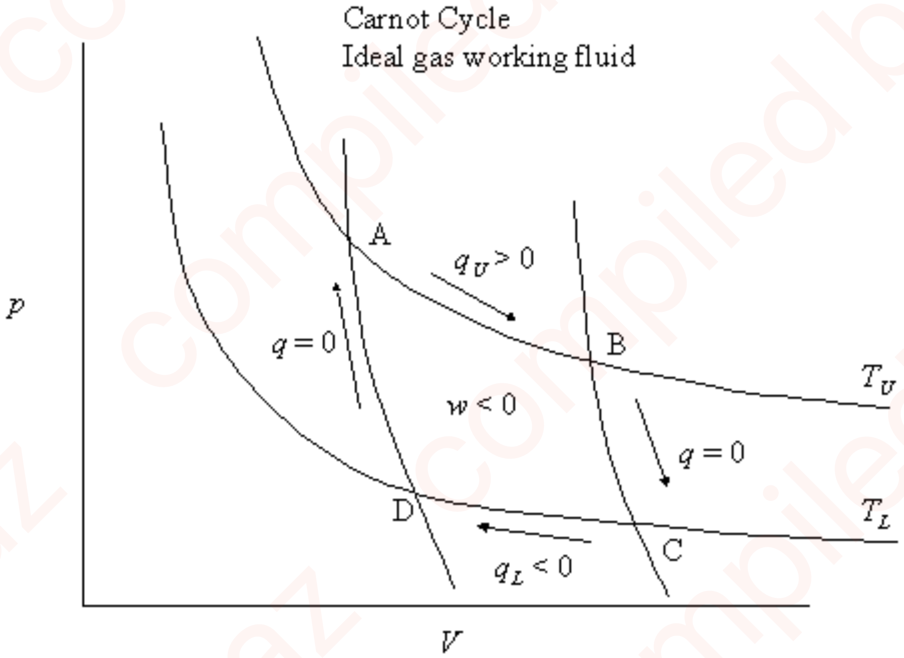
One further comment. We have seen processes where heat is converted into work before. The isothermal reversible expansion



of an ideal gas is such a process. Recall that the work is the negative of the area under the curve. However, this is not a cyclic process. A change has taken place: the volume has increased and the pressure has decreased. In order to get more work out of the system you would have to expand the gas even further. This is *not* a process in which heat was converted into work and nothing else happened.

## Heat Engines and the Carnot Cycle

A heat engine is a cyclic process that absorbs heat and does work on the surroundings. "Cyclic" means that the system returns to its initial state at the end of each cycle so that there is no permanent change in the system. The only cycle we will work with in this course is the Carnot Cycle which is shown below on a $p$-$V$ diagram.



The curves labeled $T_U$ and $T_L$ are isotherms. $T_U$ is the temperature of the upper temperature heat bath (reservoir) and $T_L$ is the temperature of the lower temperature heat bath. The two steep curves, BC and DA, are adiabatic curves. The cycle begins at the point A. The system undergoes an isothermal expansion at temperature, $T_U$ , to point B. In this isothermal expansion the system absorbs heat from the upper heat bath ($q_U > 0$) and does work on the surroundings (recall that $w$ is defined as work done on the system so $w_{AB} < 0$). The system is then isolated from the heat bath and is expanded adiabatically to the point C. There is no heat in this adiabatic expansion, but the work for this step is also negative ($w_{BC} < 0$). At point C the system is placed in contact with a heat bath at $T_L$ and undergoes an isothermal compression to point D. For this segment of the cycle $q_L < 0$ and $w_{CD} > 0$ because the surroundings are now doing work *on* the system and heat is being dissipated to the heat bath at $T_L$. At point D the system is again isolated from the heat baths and compressed adiabatically to point A. In this adiabatic compression the heat, of course, is zero and the work is positive ($w_{DA} > 0$)

We can analyze the Carnot cycle as follows: The heat, $q$, for the whole cycle is

(1) $$q = q_{AB} + q_{CD},,$$

and the work for the entire cycle is,

(2) $$w = w_{AB} + w_{BC} + w_{CD} + w_{DA} .$$

Since the initial state of the cycle is the same as the final state we know that the change in $U$, the internal energy, is zero. (That's part of the first law, because the first law says that $U$ is a state function, which means that the value of $U$ for any state of the system does not depend on how the system got to that state, only on what the state actually is.) The first law of thermodynamics then tells us that

(3) $$\Delta U = q + w = 0,$$

from which we see that

(4) $$q = -w.$$

Notice that when the Carnot cycle is operating as a heat engine (going around clockwise), $w < 0$, so that $-w > 0$ and $q > 0$.

As we have said, the Carnot cycle is a heat engine. That means that we want it to absorb heat and convert that heat energy into work. We certainly should care about how much work we get out for the heat we absorb. Thus we will define the efficiency, $e$, of a cycle as

(5) $$e = \frac{-w}{q_{AB}},$$

which, when combined with Equations 1 and 4 gives

(6) $$e = \frac{q_{AB} + q_{CD}}{q_{AB}}$$

In order to conform to the usual notation we note that the A→ B segment of the cycle is at the temperature of the upper heat bath, $T_U$, and the segment C→ D is at the temperature of the lower heat bath, $T_L$. Thus equation 6 becomes

(7) $$e = \frac{q_U + q_L}{q_U} = 1 + \frac{q_L}{q_U}$$

The A→ B and C→ D segments are an isothermal expansion of an ideal gas at $T_U$ and an isothermal compression at $T_L$, respectively. For isothermal expansions and compressions of ideal gases, $\Delta U = q + w = 0$. Thus we can write

(8) $$q_U = -w_{AB} = +nRT_U \ln \frac{V_B}{V_A}$$

and

(9) $$q_L = -w_{CD} = +nRT_L \ln \frac{V_D}{V_C}$$

Let's plug these heats into Equation 7, (right hand side) to get,

(10) $$e = 1 + \frac{nRT_L \ln \frac{V_D}{V_C}}{nRT_U \ln \frac{V_B}{V_A}}.$$

The *nR* cancels leaving,

(11) $$e = 1 + \frac{T_L \ln \frac{V_D}{V_C}}{T_U \ln \frac{V_B}{V_A}}.$$

If we are looking for an expression for efficiency in terms of temperatures Equation 11 won't do the job because of all the volumes in the equation. However, there is another set of relations between the volumes from the fact that the paths B→ C and D→ A are adiabatic and we know the volume relationships for adiabatic processes in an ideal gas. Recall that for an adiabatic expansion of an ideal gas we had the expression (using the temperatures, pressures, and volumes appropriate to our Carnot cycle here)

(12) $$p_B V_B^{\gamma} = p_C V_C^{\gamma}$$

for the B→ C segment of the cycle and a similar equation for the D→ A segment. (Recall that $\gamma$ is the "heat capacity ratio," $C_p/C_V$.) Let us eliminate the pressures from Equation 12 by inserting the value of pressure from the ideal gas equation of state, remembering that at points A and B the temperature is $T_U$ and at points C and D the temperature is $T_L$.

(13) $$\frac{nRT_U}{V_B} V_B^{\gamma} = \frac{nRT_L}{V_C} V_C^{\gamma}.$$

Cancel *nR* from both sides and combine the volumes to get,

(14) $$T_U V_B^{\gamma-1} = T_L V_C^{\gamma-1}$$

From which we obtain

(15) $$\frac{T_U}{T_L} = \frac{V_C^{\gamma-1}}{V_B^{\gamma-1}}$$

Note that there is an equivalent expression for the D→ A leg of the cycle,

(16) $$\frac{T_U}{T_L} = \frac{V_D^{\gamma-1}}{V_A^{\gamma-1}}.$$

From these two last equations we conclude that

(17) $$\frac{V_C^{\gamma-1}}{V_B^{\gamma-1}} = \frac{V_D^{\gamma-1}}{V_A^{\gamma-1}},$$

or

(18) $$\frac{V_C}{V_B} = \frac{V_D}{V_A}$$

or, on rearranging,

(19) $$\frac{V_A}{V_B} = \frac{V_D}{V_C}.$$

We now apply this result to Equation 11 to get,

(20) $$e = 1 + \frac{T_L \ln \frac{V_A}{V_B}}{T_U \ln \frac{V_B}{V_A}}.$$

The two logarithms are the negatives of each other so we conclude that,

(21) $$e = 1 - \frac{T_L}{T_U} = \frac{T_U - T_L}{T_U}$$

.

Notice that the highest efficiencies are obtained with a low temperature for the heat bath at $T_L$ and that you could only obtain unit efficiency if the lower heat bath were at absolute zero. Since, in most cases, $T_L$ is constrained by the surroundings engineers try to use the highest feasible operating temperature, $T_U$ . Real heat engines, of course, are not Carnot cycles, but the second law of thermodynamics requires that no heat engine operating between $T_U$ and $T_L$ can have an efficiency greater than a Carnot cycle efficiency. So the Carnot cycle provides an idealized upper limit to the efficiency of heat engines. Even though the Carnot cycle is idealized the general principles of heat engines remain the same. If your lower temperature, $T_L$, is constrained (by design or operating considerations) you can increase the efficiency of your heat engine by increasing $T_U$. If your upper temperature, $T_U$, is constrained you can increase the efficiency by lowering $T_L$.

You may have noticed that all of our temperatures are ideal gas temperatures. That is,they are measured on the ideal gas temperature scale. It is possible, and desirable to use the Carnot cycle to define a "thermodynamic temperature scale." We will not do this here. Suffice it to say that by choosing a suitable reference temperature you can make the two scales identical.

## Second Law of Thermodynamics - Two Cycles

We have seen that the Carnot cycle, a reversible heat engine with an ideal gas working fluid, has an efficiency,

(1)

Is this the best we can do? Does there exist another cycle which has an efficiency greater than the efficiency of the Carnot cycle? We will now show that if such a cycle exists, with an efficiency greater than a Carnot cycle, then both of our word statements of the second law will be violated. That is, if a cycle (a heat engine working between the two heat reservoirs at $T_U$ and $T_L$) exists with an efficiency greater than the efficiency of a Carnot cycle, then we can see heat spontaneously moving from a low temperature to a higher temperature with no other effect, *and* we will be able to convert heat quantitatively into work with no other effect.

Let us call the cycle with higher efficiency the "better" cycle and just say about it that it has an efficiency, *e*', which is greater than *e*.

We will set up the two cycles such that the "better" cycle drives the Carnot cycle. That is, the "better" cycle will be operated as a heat engine and it will drive the Carnot cycle which then operates as a heat pump. We know that $\Delta U = 0$ for each cycle independently and for the sum of the two cycles. Then,

(2)

or

(3)

We can adjust each cycle to alter the various $q'$s and $w'$s by changing where the adiabatic curves intersect the isotherms. Changing the positions of the adiabatic lines changes the area enclosed by the cycle and also changes the heats absorbed and released on the isothermal lines.

As we have said, in both of our two experiments the "better" cycle runs clockwise - as an engine, and the Carnot cycle runs counterclockwise as a heat pump. The engine drives the heat pump. Some or all of the work produced by the "better" cycle is used to run the (Carnot cycle) heat pump.

**Experiment 1**

Adjust the parameters of the two cycles such that $w' + w = 0$. That is, the work produced by the "better" cycle is entirely used up to drive the Carnot heat pump. This also means that there is no net work either on the system or on the surroundings. Then,

$w = -w'$,

which we can use in the expressions for the efficiencies,

(4a, b)

In Equation 4b use the fact that $w = -w'$ on the left-hand-side. For the right-hand-side, use the fact that $q_U$ is negative and move the negative side to the denominator so that both numerator and denominator are positive on the right. Then,

(4a, b, c)

In Equation (4c) $w$ is positive so we can divide both sides by $w$ without affecting the inequality.

(5,a b)

since both $q'_U$ and $-q_U$ are positive. Then,

(6)

If you were to stand back and take a look at the overall effect of this experiment, including both cycles, you would see that, according to Equation (6), heat is being released into the heat bath at the upper temperature. This is heat that must have been absorbed from the heat bath at the lower temperature because of the first law and as indicated in Equation (3). However, we also know that there is no net work being done on the two systems. The work of the "better" cycle is entirely used up driving the Carnot cycle. It appears, looking at the overall effect, that heat is spontaneously disappearing from the lower temperature heat bath and appearing in the upper temperature heat bath and there is no other effect. This violates our first word statement of the second law.

**Experiment 2**

This time adjust the parameters of the experiment so that heat given to the lower temperature heat bath by the "better" cycle is exactly balanced by the heat absorbed at the lower temperature by the Carnot cycle. That is, set

(7)

This time we find that

(8a, b, c, d)

Invert (8d) to get

(9a,b)

Recall that, by construction of Experiment 2, we have from Equation (7),

(10)

Equation (9b) becomes

(11a, b, c)

The net effect is that heat has been absorbed at the upper temperature and work has been done on the surroundings, but there was no net heat transferred to the lower temperature heat bath. This violates the second word statement of the second law. If we regard the two cycles as one large heat engine, then that engine has no "radiator." It would be nice if such an arrangement would work, and from time to time people propose schemes which are designed to make it work, but it appears that nature does not allow it.

**Conclusion**

The initial assumption that we can find another cycle, with an efficiency, *e'*, better than the Carnot cycle efficiency, leads to a contradiction of both word statements of the second law. We are forced to conclude that no cycle can have an efficiency greater than the efficiency of a Carnot cycle. That is

. (12)

Equation (12) is useful and has a number of interesting and important consequences, but it does not yet provide us with the most significant result of the second law. On the next page we will use Equation (12) to define a new state function, *S*, called "entropy," and write the second law in a mathematical form which will give us enormous new calculating power.

## The Second Law of Thermodynamics - The Equation

We have seen that there are two word statements of the second law of thermodynamics. Both statements are just statements of universal observation. That is, no one has ever observed a violation of these statements and no one expects that a violation ever will be observed. As we did with the first law, we elevate these statements to the status of a "law" and assume that they are universally valid. Then we derive the consequences of this law, which can be checked out by experiment. So far, within the domain of its validity, no one has ever observed a violation of the second law, and its consequences are consistent with experimental observation.

Recall that the word statements of the second law are:

1. Heat does not move spontaneously from a cold body to a hot body with no other effect.

2. You can not convert heat quantitatively into work with no other effect.

The first statement is pretty obvious. Heat flows from hot bodies to cold bodies not the other way around. It would be very startling if all of the heat in your pencil spontaneously flowed into the eraser end so that the eraser melted and caught fire. The second statement is probably not so obvious unless you are an engineer, but it is one of the reasons that automobiles have radiators. In practice it means that you can't convert heat into work without dissipating some of the heat into a heat bath at a lower temperature than your heat source.

We demonstrated on the previous page that both of these statements lead to the conclusion that no heat engine can have an efficiency greater than a Carnot cycle.

(Recall that the efficiency of a cycle operating as a heat engine between two heat baths, one at an upper temperature, $T_U$, and the other at a lower temperature, $T_L$, can be written in several ways. For the Carnot cycle we can write,

$$e \equiv \frac{-w}{q_U} = \frac{T_U - T_L}{T_U} = 1 - \frac{T_L}{T_U} = \frac{q_U + q_L}{q_U} = 1 + \frac{q_L}{q_U}. \qquad (1)$$

Likewise, for some other cycle, which we will indicate by putting a prime on the heats and work - still operating between $T_U$ and $T_L$ - we can write,

$$e' \equiv \frac{-w'}{q'_U} = \frac{T_U - T_L}{T_U} = 1 - \frac{T_L}{T_U} = \frac{q'_U + q'_L}{q'_U} = 1 + \frac{q'_L}{q'_U}. \qquad (2)$$

We are now considering the cycles to be operating as heat engines (as opposed to refrigerators, or heat pumps) - going around the cycle clockwise, so that $w$ and $w'$ are negative, $q_U$ and $q'_U$ are positive, and $q_L$ and $q'_L$ are negative. (We will need to know the signs of these quantities in order to carry out the algebra of inequality signs.)

Since we know from the second law that no cycle can have an efficiency greater than a Carnot cycle, we can write,

$$e' \leq e \qquad (3)$$

(We might ask what circumstances might cause the efficiency of an engine to decrease. The most obvious answer is that irreversibility, for example, friction, would cause the efficiency to go down. If there is any irreversibility in the cycle its efficiency will be degraded.)

Using our various expressions for the efficiency, Equations 1 and 2, we can rewrite equation 3 as

$$e' = 1 + \frac{q'_L}{q'_U} \leq e = 1 - \frac{T_L}{T_U}, \qquad (4)$$

or,

$$\frac{q'_L}{q'_U} \leq -\frac{T_L}{T_U}. \qquad (5)$$

Multiply both sides of Equation 5 by − 1, which reverses the inequality,

$$\frac{-q'_{\mathrm{L}}}{q'_{\mathrm{U}}} \geq \frac{T_{\mathrm{L}}}{T_{\mathrm{U}}} \quad . \qquad (6)$$

In Equation 6 we have purposely associated the minus sign with the $q'_{\mathrm{L}}$ which makes both the numerators and denominators of both sides positive. With all quantities in this equation positive we can cross-multiply at will without worrying about the direction of the inequality. Cross-multiplying we get

$$\frac{-q'_{\mathrm{L}}}{T_{\mathrm{L}}} \geq \frac{q'_{\mathrm{U}}}{T_{\mathrm{U}}} \quad , \qquad (7)$$

or

$$0 \geq \frac{q'_{\mathrm{U}}}{T_{\mathrm{U}}} + \frac{q'_{\mathrm{L}}}{T_{\mathrm{L}}} \quad . \qquad (8)$$

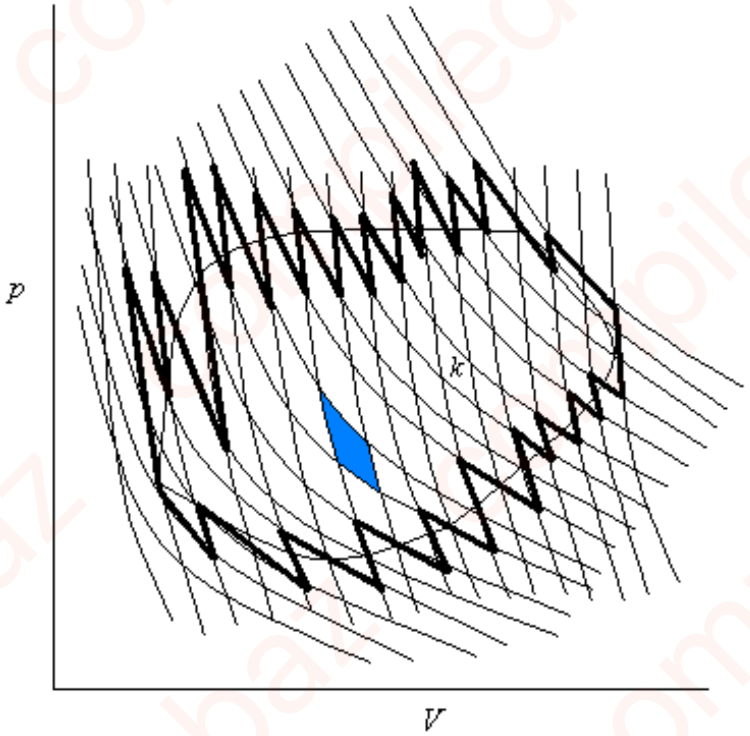
The equal sign holds when the cycle is fully reversible and "greater than" sign holds if there is any irreversibility in the cycle. In the case where the cycle is fully reversibly, then,

$$\frac{q'_{\mathrm{U,rev}}}{T_{\mathrm{U}}} + \frac{q'_{\mathrm{L,rev}}}{T_{\mathrm{L}}} = 0 \quad . \qquad (9)$$

This latter equation makes it look like,

$$\sum_{\mathrm{cycle}} \frac{q_{\mathrm{rev}}}{T} = 0 \quad . \qquad (10)$$

(Recall that two of the "legs" of the cycle were adiabatic so that there is no reversible heat on those legs.) We can generalize Equation 10 to an arbitrary closed path in $p$, $V$ space by noting that we can fill an arbitrary closed path with a large number of small Carnot cycles (an infinite number in the limit of small cycles).



When we sum over all the cycles inside the heavy line the inside "lines" of the cycles (for example the blue filled Carnot cycle in the center) will cancel because each inside line is traversed once clockwise and once counterclockwise. Therefore, only the outside lines (the heavy lines) remain. If we index the (small) cycles making up the complete cycle, by an index, *k*, where *k* ranges over all the cells inside the heavy line, this gives,

$$\sum_{\text{all cycles, } k} \frac{q_k}{T_k} = \sum_{\text{outside lines, } k} \frac{q_k}{T_k} \leq 0 \quad . \qquad (11)$$

In the limit where we approximate our arbitrary closed path by making the isotherms and adiabatic lines closer and closer together to create an infinite number of cycles, the summation in Equation 11 becomes,

$$\oint_{\text{closed path}} \frac{dq}{T} \leq 0 \quad . \qquad (12)$$

The equal sign holds when the entire path is reversibly,

$$\oint_{\text{closed path}} \frac{dq_{\text{rev}}}{T} = 0 \quad . \qquad (13)$$

This equation says that the integral of reversible heat over temperature around a closed path is zero. Equation 13 is independent of the shape of the path - as long as it is a closed loop - which implies that,

$$\frac{dq_{\text{rev}}}{T} \qquad (14)$$

is the differential of a state function. We will call this state function entropy and give it the symbol, *S*. Equation 14 becomes

$$dS = \frac{dq_{\text{rev}}}{T}. \qquad (15)$$

Combining Equations (12), (13), and (15) we get,

$$\oint_{\text{closed path}} \frac{dq}{T} \leq \oint_{\text{closed path}} \frac{dq_{\text{rev}}}{T} = \oint_{\text{closed path}} dS. \qquad (16)$$

Since the closed path is arbitrary, Equation (16) must be valid for any possible closed path. The only way this can be true is if the equation is true in its differential form. That is,

$$\frac{dq}{T} \leq \frac{dq_{\text{rev}}}{T} = dS, \qquad (17)$$

which can be rewritten as simply

$$\frac{dq}{T} \leq dS, \qquad (18)$$

or, the best way to remember it,

$$dS \geq \frac{dq}{T}, \qquad (19)$$

with the understanding that the equal sign holds when the process is reversible and the greater-than sign holds when the process is irreversible.

Equation (19) is the second law of thermodynamics in equation form. Equation (18) would work just as well, but most of us would prefer (19) because it is in the form of a definition of *dS*.

## Second Law Applications - Equilibrium and Entropy Changes

### Fundamental Definition of Equilibrium

The second law of thermodynamics in equation form is,

$$dS \geq \frac{dq}{T}, \qquad (1)$$

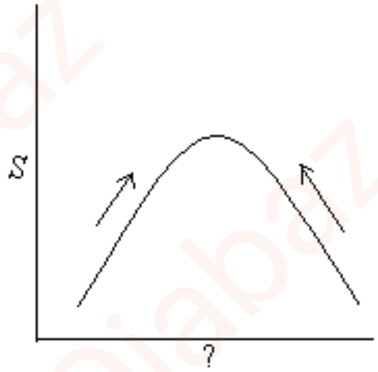
where the = sign holds when the process is reversible and the > holds when it is irreversible. Our first application of the second law will be to provide a thermodynamic definition of equilibrium. We indicated very early in the course that at equilibrium none of the variables was changing in time. (Of course, a system in a steady state has to be excluded from this definition.) Another possible definition of equilibrium was that all the variables have the values they would have at time equals infinity. Neither of these "definitions" provides an equation we can use to discuss equilibrium systems carefully.

The second law provides us with a definition of equilibrium that we can use to derive equilibrium properties of thermodynamic systems. Consider a closed isolated system. In a closed isolated system $dq = 0$ and $dV = 0$ which implies that $dU = 0$. (Actually, we should really say that $dw$ for all forms of work are zero, but for the time being we will only consider $pV$ work.)

Under the conditions of constant $U$ and $V$ the second law, Equation 1, becomes

$$dS_{U,V} \geq 0. \qquad (2)$$

This may look simple, but it is a very profound statement. It says that in a closed isolated system (a system which us not being disturbed from the outside) any spontaneous change must increase the entropy.
In a closed, isolated system the entropy seeks a maximum.



If you plot the entropy of a closed isolated system against some system variable any spontaneous change in the system must take the system to higher entropy. If the system is not in equilibrium then

$$dS_{U,V} > 0,$$

but if the system is at equilibrium any spontaneous change in the system must leave the entropy unchanged,

$$dS = 0.$$

Equation 2 is the origin of the somewhat arrogant statement that you may have heard, "The entropy of the universe is increasing." If you regard the universe as a closed isolated system then the statement is probably true, even though it is difficult to take such broad statements concerning the nature of the universe seriously.

## Combined First and Second Laws

The first thing we must do is incorporate our new-found equation for the second law into what we already know. Going back to the first law, with $pV$ work only, recall that we can write

$$dU = dq - pdV. \qquad (3)$$

If we restrict our attention to reversible processes this becomes,

$$dU = dq_{rev} - pdV, \qquad (4)$$

but we know from the second law that

$$dq_{\text{rev}} = TdS. \qquad (5)$$

Merging Equations 4 and 5 we arrive at what is called the combined first and second laws,

$$dU = TdS - pdV. \qquad (6)$$

(Later on, when we want to include work other than $pV$ work, we will add it in to Equation 6,

$$dU = TdS - pdV + dw_{\text{other}}, \qquad (7)$$

but for now we will just stick with $pV$ work.)

Equation 6 implies that the natural variables of internal energy, $U$, are $S$ and $V$. In previous calculations we have regarded $U$ and a function of $T$ and $V$ or of $T$ and $p$, but nature - in the form of the first and second laws of thermodynamics - gives us $U$ as a function of $S$ and $V$.

Divide Equation 6 by $dT$ and hold $V$ constant:

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V + 0 = C_V$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}. \qquad (8a, b)$$

Equation 8b provides us with a way to calculate entropy changes for a certain class of processes, namely processes at constant volume. Set up Equation 8b for integration,

$$dS_V = \frac{C_V}{T}dT, \qquad (9)$$

and calculate the entropy change for a constant volume process as,

$$\Delta S_V = \int_{T_1}^{T_2} \frac{C_V}{T}dT. \qquad (10)$$

Continuing to incorporate the second law into our set of thermodynamic tools, recall that

$$H = U + pV$$

$$dH = dU + pdV + Vdp$$

$$dH = TdS - pdV + pdV + Vpd$$

$$dH = TdS + Vdp. \qquad (11a, b, c, d)$$

(Note that equation 11d implies that the natural variables of $H$ are $S$ and $p$.)

This time let's divide Equation 11d by $dT$ and hold $p$ constant,

$$\left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p + 0 = C_p$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}. \qquad (12a, b)$$

We can use Equation 12b to calculate entropy changes for processes at constant pressure. Set up Equation 12b for integration,

$$dS_p = \frac{C_p}{T} dT, \tag{13}$$

and integrate,

$$\Delta S_p = \int_{T_1}^{T_2} \frac{C_p}{T} dT. \tag{14}$$

What about processes at constant *T*? We can calculate the entropy change for a process at constant temperature by rearranging Equation 5 for integration,

$$dS = \frac{dq_{\text{rev}}}{T}. \tag{15}$$

The finite entropy change is,

$$\Delta S = \int \frac{dq_{\text{rev}}}{T}. \tag{16}$$

If we now restrict consideration to processes at constant *T* Equation 16 becomes,

$$\begin{aligned} \Delta S_T &= \int \frac{dq_{T,\text{rev}}}{T} \\ &= \frac{1}{T} \int dq_{T,\text{rev}} \\ &= \frac{q_{T,\text{rev}}}{T}. \end{aligned} \tag{17}$$

**Example Calculation**

Calculate the entropy change in heating 1.00 mol of Al from 300 K to 500 K at constant pressure. The constant pressure heat capacity of Al is given to good approximation by,

$$C_p = 20.67 \frac{\text{J}}{\text{Kmol}} + 12.38 \times 10^{-3}\, T \frac{\text{J}}{\text{K}^2\text{mol}}.$$

The calculation is

$$\begin{aligned} \Delta S_p &= \int_{T_1}^{T_2} \frac{C_p}{T} dT = \int_{T_1}^{T_2} \frac{20.67}{T} dT + \int_{T_1}^{T_2} 12.38 \times 10^{-3} dT \\ &= 20.67 \ln \frac{500\ \text{K}}{300\ \text{K}} + 12.38 \times 10^{-3} (500\ \text{K} - 200\ \text{K}) \\ &= 13.04 \frac{\text{J}}{\text{K}}. \end{aligned}$$

**Another Example - An irreversible Process**

Often we must calculate entropy changes for irreversibly processes. We don't know how to calculate entropy changes for irreversible processes, but it doesn't matter. Entropy is a state function so $\Delta S$ is independent of path. All we have to do is imagine a reversible path which will effect the same change and calculate the entropy change for the reversibly path.

Suppose we start with a 100. g block of Cu at 500 K and a 100. g block of Cu at 300 K. Bring the two blocks into thermal contact and heat will flow from the hotter block to the cooler block until they reach the same temperature. This is definitely an irreversible process. However, let's imagine that we can reversibly cool the hot Cu block down to the final temperature and reversibly warm the cold Cu block up to the final temperature. We can calculate the entropy change for both of these processes from Equation (14). The total entropy change is just the sum of the two individual entropy changes. Note that we expect the entropy for this process to be positive because the process is spontaneous and the two Cu-block system can be regarded as isolated.

We need the following data:

$$C_{p,\mathrm{m,Cu}} = 22.64\,\frac{\mathrm{J}}{\mathrm{K}}$$

$$\mathrm{FW_{Cu}} = 63.5\,\frac{\mathrm{g}}{\mathrm{mol}}$$

First we must find the final temperature. We do this by recognizing that the heat lost by one Cu block is gained by the other Cu block. This is called "heat balance."

$$\frac{100\ \mathrm{g}}{63.5\,\frac{\mathrm{g}}{\mathrm{mol}}}\,22.64\,(500 - T_{\mathrm{fin}}) = \frac{100\ \mathrm{g}}{63.5\,\frac{\mathrm{g}}{\mathrm{mol}}}\,22.64\,(T_{\mathrm{fin}} - 300).$$

This is easily solved to obtain $T_{\mathrm{fin}} = 400$ K. Then

$$\Delta S_1 = \frac{100\ \mathrm{g}}{63.5\,\frac{\mathrm{g}}{\mathrm{mol}}} 22.64 \ln \frac{400\ \mathrm{K}}{500\ \mathrm{K}} = -7.95\,\frac{\mathrm{J}}{\mathrm{K}}$$

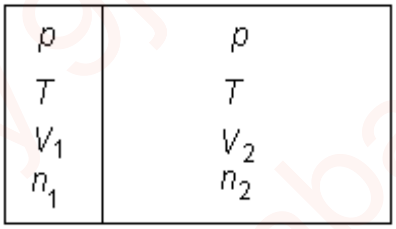
$$\Delta S_2 = \frac{100\ \mathrm{g}}{63.5\,\frac{\mathrm{g}}{\mathrm{mol}}} 22.64 \ln \frac{400\ \mathrm{K}}{300\ \mathrm{K}} = +10.25\,\frac{\mathrm{J}}{\mathrm{K}}$$

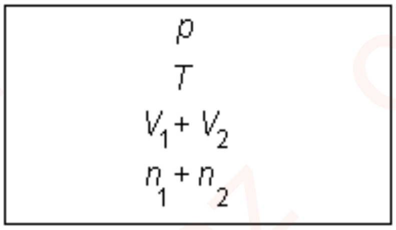
$$\Delta S = \Delta S_1 + \Delta S_2 = 2.30\,\frac{\mathrm{J}}{\mathrm{K}}.$$

## Second Law Applications - Equilibrium and Entropy Changes

### Entropy of Mixing (Ideal Gases)

Visualize that we have a container divided into two compartments. In one compartment we have $n_1$ moles of an ideal gas, gas 1, at pressure, $p$ and temperature, $T$. In the other compartment we have $n_2$ moles of another ideal gas, gas 2, at the same $p$ and $T$.





If we remove the partition the gases will begin to diffuse into each other and the system will eventually reach the state where both gases are uniformly distributed throughout the container. This is clearly an irreversibly process so that we would expect that the entropy would increase.

To calculate the entropy change we must find a reversible path to carry out the process, even if the path is fictitious. Imagine that we can devise a process that will expand one gas reversibly and isothermally, but leave the other gas undisturbed. We know how to calculate the change in entropy for the reversible isothermal expansion of an ideal gas.

Recall that $dU = 0$ for the isothermal expansion of an ideal gas. Then,

$$dU = TdS - pdV = 0. \qquad (1)$$

So,

$$
\begin{aligned}
TdS &= pdV \\
dS &= \frac{p}{T}dV \\
&= \frac{nR}{V}dV,
\end{aligned}
\tag{2a, b, c}
$$

for an ideal gas. So, for gas number 1 in our fictitious isothermal expansion we have,

$$\Delta S_1 = n_1 R \ln \frac{V_1 + V_2}{V_1}, \tag{3a}$$

and for gas number 2,

$$\Delta S_2 = n_2 R \ln \frac{V_1 + V_2}{V_2}. \tag{3b}$$

The total entropy change is the sum of these two individual entropy changes,

$$\Delta S_{\text{mix}} = \Delta S_1 + \Delta S_2 = n_1 R \ln \frac{V_1 + V_2}{V_1} + n_2 R \ln \frac{V_1 + V_2}{V_2}. \tag{4}$$

Equation 4 could be used for calculations, but it is not in the form that we will see in other contexts. To obtain the usual form factor the *R* out of Equation 4 and invert the argument of the logarithms,

$$\Delta S_{\text{mix}} = -R\left( n_1 \ln \frac{V_1}{V_1 + V_2} + n_2 \ln \frac{V_2}{V_1 + V_2} \right). \tag{5}$$

Since we are doing a calculation for ideal gases, notice that the argument of the first logarithm in Equation 5 can be written,

$$\frac{V_1}{V_1 + V_2} = \frac{\dfrac{n_1 RT}{p}}{\dfrac{n_1 RT}{p} + \dfrac{n_2 RT}{p}} = \frac{n_1}{n_1 + n_2} = X_1, \tag{6}$$

where $X_1$ is the mole fraction of component 1. There is an equivalent expression for the argument of the second logarithm. The entropy of mixing becomes,

$$\Delta S_{\text{mix}} = -R\left( n_1 \ln X_1 + n_2 \ln X_2 \right). \tag{7}$$

Equation 7 is also suitable for calculations, but it is not yet in the standard form. To obtain the standard form write the total number of moles $n_1 + n_2$ as $n$ and multiply and divide equation 7 by $n$. The result is

$$\Delta S_{\text{mix}} = -nR\left( X_1 \ln X_1 + X_2 \ln X_2 \right). \tag{8}$$

Equation 8 is the same form that we will find when we derive an expression for the entropy of mixing ideal solutions and it is the same form that Shannon found for the "entropy of a message" in his famous series of papers on information theory.

If the two gases were not at the same initial pressure you would have to introduce some extra steps. Expand or compress one of the gases to bring it to the pressure of the other gas, mix the gases, and then compress or expand the mixture to bring it to the correct final volume and pressure.

If the two gases are not at the same temperature and pressure it is more complicated. You must find the final temperature using heat balance, reversibly cool and heat the two gases respectively to the same temperature, expand or contract on of the gases, mix them, and then expand or contract the mixture to the appropriate volume.

Equation 8 can easily be extended to more than two gases,

$$\Delta S_{\text{mix}} = -nR\left( X_1 \ln X_1 + X_2 \ln X_2 + X_3 \ln X_3 + \cdots \right). \qquad (9)$$

Example - The molar entropy of dry air

The composition of dry air is approximately 78% $N_2$, 21% $O_2$, and 1% Ar by volume (which is the same as mole percent). What is the molar entropy of mixing of air?

$$\Delta S_{\text{mix,air}} = 1\ \text{mol} \times 8.314 \frac{\text{J}}{\text{K mol}} \left(0.78 \ln 0.78 + 0.21 \ln 0.21 + 0.01 \ln 0.01)\right)$$

$$= 4.7 \frac{\text{J}}{\text{K}}.$$

**What Does Entropy Measure?**

Entropy measures disorder.

If we look at the processes we have seen which have positive entropy changes we can see that in each case an increase in entropy is associated with an increase in disorder.

An isothermal expansion gives the molecules more room to move around in, the molecules are less localized.

Increasing the temperature increases the average speeds of the molecules. The molecules are said to be more disordered in "velocity space" (or momentum space).

Mixing gases (or liquids) intersperses the molecules among each other increasing the disorder.

Phase changes, such as going from a solid to a liquid or a gas, or from a liquid to a gas, increase the entropy because gases are more disordered than solids or liquids and liquids are more disordered than solids.

For example, the entropy of fusion of 1.00 mol of ice at 273.15 (heat of fusion is 6.008 kJ/mol) is

$$\Delta S_{\text{fus}} = \frac{6008\ \text{J}}{273.15\ \text{K}} = 22.0\frac{\text{J}}{\text{K}}.$$

Vaporization of liquids has a large positive entropy of vaporization because gases are greatly disordered compared to liquids. A typical value is obtained from the vaporization of benzene at its boiling point. The heat of vaporization is 30.8 kJ at the boiling point, 353.1K. The entropy of vaporization is

$$\Delta S_{\text{vap}} = \frac{30800\ \text{J}}{353.1\ \text{K}} = 87.2\frac{\text{J}}{\text{K}}.$$

It is interesting that the entropy of vaporization of many substances at their boiling points is close to about 86 J/K. (Water and helium are exceptions.) This phenomenon is called "Trouton's rule." It is easily understood on the basis of entropy being a measure of disorder. The vaporization process essentially "creates" a mole of disordered molecules (the gas) from a mole of highly ordered molecules (the solid or liquid). The gases are all at one atmosphere pressure because we are at their normal boiling point.

## Some Tools of Thermodynamics

### Some Miscellaneous Relationships

Recall that the combined first and second laws give the relationship

$$dU = TdS - pdV. \tag{1}$$

This implies that *U* is a function of *S* and *V*. Sometimes we call *S* and *V* the "natural variables" of *U*. Regarding $U = U(S,V)$ we can write

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV. \tag{2}$$

Comparing Equations 1 and 2 it is clear that

$$\left(\frac{\partial U}{\partial S}\right)_V = T, \tag{3a}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -p. \tag{3b}$$

These two equations can be regarded as thermodynamic definitions of *T* and *p*.

Likewise, from the definition of enthalpy we wrote before that

$$dH = TdS + Vdp. \tag{4}$$

Equation 4 implies that enthalpy is a natural function of *S* and *p*. Regarding $H = H(S,p)$ we can write

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp. \tag{5}$$

From Equations 4 and 5 it is clear that

$$\left(\frac{\partial H}{\partial S}\right)_p = T, \tag{6a}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_S = V. \tag{6b}$$

Equations 6a and 6b give us another thermodynamic definition of *T* and a thermodynamic definition of *V* (which is curious since we have always regarded *V* as a purely mechanical variable).

## Helmholtz and Gibbs Free Energy

When we made the transformation from *U* to *H* by the Legendre transformation,

$$H = U + pV, \tag{7}$$

we remarked that *V* was not the most convenient independent variable. In the laboratory it is usually much easier to control pressure than it is to control *V*. Since both *U* and *H* are natural functions of entropy, it is fair to ask how convenient it is to have *S* as a variable. The answer is that it is not at all convenient to control entropy or to have entropy as an independent variable. We do not have a meter that reads entropy and we do not know how to hold entropy constant as we change some other variable. (Recall that we can control temperature, pressure, and volume.) So we make some more Legendre transformations.

(We will not give an extensive discussion of Legendre transformations here, but we should point out that they are not arbitrary. You can't just pick any two variables you wish and put them together to make a Legendre transformation. We could make the Legendre transformation from *U to H* by adding the *pV* term to *U* only because *V* is related to p and *U* through Equation 3b. Using this as a guide it would seem reasonable to use Equation 3a to change the variable *S* to *T* in the function *U*, and use Equation 6a to change the variable *S* to *T* in the function *H*. Let's try it.)

Define the Helmholtz free energy, *A*, as

$$A \equiv U - TS. \tag{8}$$

Then,

$$\begin{aligned} dA &= dU - TdS - SdT \\ &= TdS - pdV - TdS - SdT \\ &= -SdT - pdV. \end{aligned}$$ (9a, b, c)

Equation 9c tells us that the Helmholtz free energy is a natural function of *T* and *V*. That is, $A = A(T,V)$. *T* and *V* are much more convenient variables than *S* and *V*. Regarding $A = A(T,V)$ we see that

$$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV.$$ (10)

Now compare Equation 10 with Equation 9c to see that,

$$\left(\frac{\partial A}{\partial T}\right)_V = -S,$$ (11a)

and

$$\left(\frac{\partial A}{\partial V}\right)_T = -p.$$ (11b)

Equation 11a gives us a thermodynamic definition of entropy and 11b gives another thermodynamic definition of pressure.

We now have a function of *T* and *V*, but we didn't much like *V* as an independent variable before so why should we like it any better now? Let's use the relationship 6a to define the Gibbs free energy, *G*, as,

$$G \equiv H - TS.$$ (12)

Actually, we can use any one of the three equivalent definitions,

$$\begin{aligned} G &= H - TS \\ G &= A + pV \\ G &= U + pV - TS. \end{aligned}$$ (13a, b, c)

Any one of Equations 13a, b, or c will give us the correct natural variables of *G*. Use Equation 12.

$$\begin{aligned} dG &= dH - TdS - SdT \\ &= TdS + Vdp - TdS - SdT \\ &= -SdT + Vdp. \end{aligned}$$ (14a, c, c)

From Equation 14c we see that the natural variables of *G* are temperature and pressure. Write

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp.$$ (15)

Comparing Equation 15 with Equation 14c we find that.

$$\left(\frac{\partial G}{\partial T}\right)_p = -S, \qquad (16a)$$

and

$$\left(\frac{\partial G}{\partial p}\right)_T = V. \qquad (16b)$$

Equation 16a gives us another thermodynamic definition of entropy and 16b another definition of volume.

## Meaning of *A* and *G*

What do *A* and *G* mean and what are they good for? We said after the introduction of the first law (which introduced the internal energy, *U*) that we would be introducing three more functions that have units of energy. We now know that these functions are *H*, *A*, and *G*. At the time we said that only *U* has a simple physical meaning - the sum of all the kinetic and potential energies of all the particles. There is no simple physical explanation for enthalpy and the two free energies. The best we can do is tell how they are used.

1) Most simple-minded.

Set

$$dU = TdS - pdV + dw_{\text{other}}. \qquad (17)$$

Then, using the definition of Helmholtz free energy as we have done above we find that,

$$dA = -SdT - pdV + dw_{\text{other}}. \qquad (18)$$

For any process at constant temperature we have,

$$dA_T = -pdV + dw_{\text{other}} = dw_{\text{all, reversible}}. \qquad (19)$$

That is, for a constant temperature process the Helmholtz free energy gives all the reversible work. For this reason the Helmholtz free energy is sometimes called the "work function." When a physicist says "free energy" without indicating Helmholtz or Gibbs, he usually means Helmholtz free energy.

Similarly, we can write,

$$dG = -SdT + Vdp + dw_{\text{other}}. \qquad (20)$$

For a process at constant temperature *and* pressure we get,

$$dG_{T,p} = dw_{\text{other}} = dw_{\text{all, non-pV}}. \qquad (21)$$

That is, for a process at constant temperature and pressure the change in Gibbs free energy gives all the reversible work except the *pV* work. This work might include electrical work, work creating surface area, and so on. Chemists do most of their reactions on the bench top at constant pressure. When a chemist says "free energy" she almost always means Gibbs free energy unless she specifically states otherwise.

2) More useful - two new criteria for equilibrium

Recall that the second law of thermodynamics,

$$dS \geq \frac{dq}{T}, \qquad (22)$$

gives us the fundamental criterion for equilibrium. That is, in a closed isolated system entropy seeks a maximum,

$$dS_{U,V} \geq 0 \qquad (23)$$

Although this is the fundamental definition of equilibrium it is not the most useful definition because we do not often work with closed isolated systems. More often we work with systems at constant temperature and either constant volume or constant pressure. We can use the second law, Equation 22, and our new functions *A* and *G* to find criteria for equilibrium under these conditions.

Rewrite the second law, Equation 22 as follows:

$$\begin{aligned} TdS &\geq dq \\ 0 &\geq dq - TdS, \end{aligned} \qquad (24)$$

or

$$dq - TdS \leq 0. \qquad (25)$$

Now, going back to the original form of the first law with only *pV* work,

$$dU = dq - pdV, \qquad (26)$$

and making the transformation to Helmholtz free energy we get,

$$\begin{aligned} dA &= dU - TdS - SdT \\ &= dq - pdV - TdS - SdT \\ &= (dq - TdS) - pdV - SdT. \end{aligned} \qquad (27a, b, c)$$

For a process at constant temperature and volume we have,

$$dA_{T,V} = dq - TdS \leq 0. \qquad (28)$$

We conclude that for a process at constant temperature and volume the Helmholtz free energy seeks a minimum. Any spontaneous process in a system at constant *T* and *V* must decrease the Helmholtz free energy (if the system is away from equilibrium) or leave the Helmholtz free energy unchanged (if the system is at equilibrium).

By the same token, we can use the Gibbs free energy to discuss processes at constant temperature and pressure,

$$
\begin{aligned}
dG &= dH - TdS - SdT \\
&= dq + Vdp - TdS - SdT \\
&= (dq - TdS) + Vdp - SdT,
\end{aligned}
\tag{29a, b, c}
$$

from which we conclude that for a process at constant $T$ and $p$,

$$dG_{T,p} = dq - TdS \leq 0. \tag{30}$$

That is, at constant $T$ and $p$ the Gibbs free energy seeks a minimum. Any spontaneous process in a system at constant $T$ and $p$ must decrease the Gibbs free energy (if the system is away from equilibrium) or leave the Gibbs free energy unchanged (if the system is at equilibrium).

**Maxwell's Equations**

We now have the tools to derive some very useful relationships between thermodynamics variables. Maxwell's equations are based on the same principle as was Euler's test for exact differentials, namely that mixed second derivatives of "nice" functions must be equal. Applying this principle to our two new free energy functions we find,

$$\frac{\partial^2 A}{\partial V \partial T} = \frac{\partial^2 A}{\partial T \partial V}, \tag{31}$$

but we already know the first derivatives of $A$ from Equations 11a and 11b. So,

$$
\begin{gathered}
\frac{\partial^2 A}{\partial V \partial T} = \frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V = \frac{\partial^2 A}{\partial T \partial V} = \frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T, \\
\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V = \frac{\partial}{\partial V}(-S) = \frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T = \frac{\partial}{\partial T}(-p), \\
\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V.
\end{gathered}
\tag{32a, b, c}
$$

We obtain another similar equation from the Gibbs free energy,

$$\frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p}, \tag{33}$$

which becomes, using Equations 16a and 16b,

$$\frac{\partial^2 G}{\partial p \partial T} = \frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right)_p = \frac{\partial^2 G}{\partial T \partial p} = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)_T,$$

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

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

(34a, b, c)

There are two more Maxwell's equations from *dU* and *dH*, but these are not as useful as the ones just derived. We will leave it to the reader to find the Maxwell's equations from *dU* and *dH*.

## First Application of a Maxwell's Equation

As our first application of a Maxwell's equation we will derive the so-called thermodynamic equation of state which we stated without proof earlier. Write the combined first and second laws,

$$dU = TdS - pdV. \qquad (1)$$

Divide Equation 1 by *dV* and hold *T* constant to get,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p. \qquad (35)$$

Using the Maxwell's Equation, Equation 32c, to substitute for the entropy derivative we obtain,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p. \qquad (36)$$

Equation 36 is the equation that was written down without proof at the time we were discussing the Joule expansion.

The other version of thermodynamic equation of state, based on *H* instead of *U*, will be left as an exercise for the reader.

## Summary

We now have four interesting and useful derivatives of entropy,

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

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

There are two other derivatives of entropy which might prove useful,

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

$$= \left(\frac{C_V}{T}\right)\left(\frac{\partial T}{\partial p}\right)_V . \tag{37}$$

The other derivative, $\left(\frac{\partial S}{\partial V}\right)_p$, will be left to the reader.

## Adiabatic Compressibility

The speed of sound in a gas depends on the "springiness" of the gas. That is, it depends on how the volume of the gas responds to changes in pressure. We have already seen one measure of this response, called the isothermal compressibility,

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T . \tag{1}$$

Equation one gives a parameter that determines how the gas responds to changes in pressure if the temperature remains constant.

Sir Isaac Newton assumed that the speed of sound was an isothermal process and used the parameter defined by Equation 1 to calculate the speed of sound in a gas. His answer did not agree with experiment.

It turns out that sound transmission in a gas is an adiabatic process rather than an isothermal process. The sound wave causes oscillations in pressure but the oscillations are fast enough that heat can not move from compressed regions to rarified regions in order to keep the temperature constant. Before the heat can be conducted away from the compressed regions the compression has moved on so that sound propagation is adiabatic.

We define the adiabatic compressibility as,

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S . \qquad (2)$$

We can calculate the adiabatic compressibility in terms of quantities that we already know (using the Euler cyclic rule twice, once the normal way and once in reverse).

$$\begin{aligned}\kappa_S &= -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S \\ &= -\frac{1}{V}\left(-\frac{\left(\frac{\partial S}{\partial p}\right)_V}{\left(\frac{\partial S}{\partial V}\right)_p}\right) \\ &= -\frac{1}{V}\left(-\frac{\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial T}{\partial V}\right)_p}\right),\end{aligned} \qquad (3a, b, c)$$

where we have used Euler's cyclic relation to go from Equation 3a to 3b and the chain rule in the denominator and numerator of 3b to go to 3c.

We already know that

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{C_V}{T}\right) \qquad (4a)$$

and

$$\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{C_p}{T}\right), \qquad (4b)$$

so

$$\kappa_S = -\frac{1}{V}\left( -\frac{\left(\frac{C_V}{T}\right)\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{C_p}{T}\right)\left(\frac{\partial T}{\partial V}\right)_p} \right)$$

$$= -\frac{C_V}{C_p}\frac{1}{V}\left( -\frac{\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial T}{\partial V}\right)_p} \right). \qquad (5a, b)$$

In Equation 5b we can use Euler's cyclic rule in reverse to write

$$\kappa_S = -\frac{C_V}{C_p}\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

$$= \frac{C_V}{C_p}\kappa_T. \qquad (6a,b)$$

Since $C_p > C_V$ The isothermal compressibility is always greater than the adiabatic compressibility.

For a monatomic ideal gas, where $C_p = 5nR/2$ and $C_V = 3nR/2$ we see that

$$\kappa_S = \frac{3}{5}\kappa_T. \qquad (7)$$

**Adiabatic Gas Expansion Revisited**

Early in the course we derived the equation for the adiabatic expansion of an ideal gas,

$$pV^{\gamma} = \textbf{constant},$$

or

$$p_1V_1^{\gamma} = p_2V_2^{\gamma}, \qquad (8a, b)$$

where,

$$\gamma = \frac{C_p}{C_V}. \qquad (9)$$

You may recall that the derivation was sort of "round-about." Here we would like to use some of our new thermodynamics tools to provide a much more direct derivation.

The goal is to discover how the pressure changes with volume if entropy is held constant. That is, we would like to find the derivative,

$$\left(\frac{\partial p}{\partial V}\right)_S.$$

Then we can integrate this derivative to find an expression for $p$ as a function of $V$. First, let's find the derivative. Notice that this derivative is just the reciprocal of the derivative in Equation 2 so most of the work has already been done. Using the same procedures we used above we fin that,

$$\begin{aligned}
\left(\frac{\partial p}{\partial V}\right)_S &= -\frac{\left(\frac{\partial S}{\partial V}\right)_p}{\left(\frac{\partial S}{\partial p}\right)_V} \\
&= -\frac{\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial T}{\partial V}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial p}\right)_V} \\
&= -\frac{\frac{C_p}{T}\left(\frac{\partial T}{\partial V}\right)_p}{\frac{C_V}{T}\left(\frac{\partial T}{\partial p}\right)_V} \\
&= \frac{C_p}{C_V}\left(-\frac{\left(\frac{\partial T}{\partial V}\right)_p}{\left(\frac{\partial T}{\partial p}\right)_V}\right) \\
\left(\frac{\partial p}{\partial V}\right)_S &= \gamma\left(\frac{\partial p}{\partial V}\right)_T.
\end{aligned}$$

(10a, b, c, d, e, f)

Equation 10f is a general thermodynamic relationship. It contains no approximations. To proceed further we must decide what material we want to consider. The equation we were trying to derive was based on the ideal gas for which

$$\begin{aligned}
\left(\frac{\partial p}{\partial V}\right)_T &= -\frac{nRT}{V^2} \\
&= -\frac{p}{V}.
\end{aligned}$$

(11a, b)

So,

$$\left(\frac{\partial p}{\partial V}\right)_S = -\gamma \frac{p}{V}. \qquad (12)$$

Set up Equation 12 for integration, (don't forget to put all the *p* stuff on one side and all the *V* stuff on the other)

$$\frac{dp}{p} = -\gamma \frac{dV}{V}, \qquad (13)$$

and integrate between $p_1$, $V_1$ and $p_2$, $V_2$,

$$\int_{p_1}^{p_2} \frac{dp}{p} = -\gamma \int_{V_1}^{V_2} \frac{dV}{V}, \qquad (14)$$

where we have made the approximations that $\gamma$ is independent of volume and factored it out of the integral. Equation 14 integrates to

$$\begin{aligned} \ln \frac{p_2}{p_1} &= -\gamma \ln \frac{V_2}{V_1} \\ &= +\gamma \ln \frac{V_1}{V_2} \\ &= \ln \frac{V_1^\gamma}{V_2^\gamma}, \end{aligned} \qquad (15a, b, c)$$

from which we conclude that

$$\frac{p_2}{p_1} = \frac{V_1^\gamma}{V_2^\gamma}, \qquad (16)$$

or

$$p_1 V_1^\gamma = p_2 V_2^\gamma. \qquad (8b)$$

Just for the record, we add that the correct formula for the speed of sound is

$$v_{\text{sound}} = \frac{1}{\sqrt{\rho \kappa_S}}, \qquad (17)$$

where $\rho$ is the density of the gas (in kg/m$^3$).

## Gibbs Free Energy and Chemical Reactions

We have seen that the Gibbs free energy, *G*, seeks a minimum at constant *T* and *p*. The question now is does this have anything to do with chemical reactions. We define the change in Gibbs free energy for a chemical reaction as,

$$\Delta_r G^\circ = G_{\text{products}} - G_{\text{reactants}}. \qquad (1)$$

It is understood in Equation 1 that both the reactants and the products are pure, isolated, in their standard states, and at the same temperature and pressure.

When we first introduced heats of reaction we said that it is not feasible to tabulate the $\Delta H^\circ$ for every possible reaction. Instead, we tabulate heats of formation for compounds and use Hess' law to find the heat of a reaction involving those compounds.

In the same manner we define the Gibbs free energy of formation for a compound as $\Delta G^\circ$ for the reaction:

pure isolated elements in their standard states →

one mole of pure compound in its standard state.

For example, $\Delta_f G^\circ$ for $CO_2(g)$ at 25° and 1 atm is defined to be the $\Delta G$ for the reaction:

$C(s, \textit{graphite}) + 2\, O_2(g) \rightarrow CO_2(g)$.
Then, using Hess' law, the $\Delta_r G^\circ$ for some arbitrary reaction, say
$a\,A + b\,B \rightarrow c\,C + d\,D$, (2)
is
$\Delta_r G^\circ = c\,\Delta_f G_C{}^\circ + d\,\Delta_f G_D{}^\circ - a\,\Delta_f G_A{}^\circ - b\,\Delta_f G_B{}^\circ$. (3)
Rarely one might want to run a reaction at constant volume and, therefore, would need the change in the Helmholtz free energy. We can obtain $\Delta_r A^\circ$ using the same approximations we used to obtain $\Delta U$ from $\Delta H$. That is, from

$$G = A + pV$$

we see that,

$$\Delta A = \Delta G - \Delta(pV).$$

Using, as before, the approximation that the change in the $pV$ product for liquids and solids is small and the approximation that the gases are ideal, we obtain the equation,

$$\Delta_r A^\circ \approx \Delta_r G^\circ - RT\Delta n_{\text{gas}}. \qquad (4)$$

**Processes at Constant Temperature**

Knowing that $G = H - TS$, and that reactions are constant temperature process, we can relate the Gibbs free energy of a reaction to the enthalpy of a reaction. That is,

$$G = H - TS,$$
$$\Delta G = \Delta H - \Delta(TS)$$
$$\Delta G_T = \Delta H_T - T\Delta S_T. \qquad (5a, b, c)$$

We have written a subscript, $T$, in Equation 5c to indicate that the equation is only valid at constant $T$, but it is unusual to include the $T$. Usually we see

$$\Delta G = \Delta H - T\Delta S, \quad (6)$$

and it is left to the reader to understand that the equation is only valid at constant $T$.

## The "Driving Force" of a Chemical Reaction

Recall that at constant $T$ and $p$ the Gibbs free energy seeks a minimum. That means that we can use $\Delta_r G^o$ to tell whether or not a reaction will proceed spontaneously as written:

If $\Delta_r G^o > 0$ then the reaction will not go as written (the reverse reaction will go)

if $\Delta_r G^o < 0$ then the reaction will go as written.

Sometimes people say that $\Delta_r G^o$ is a measure of the "driving force" of a chemical reaction. Although the use of the word "force" is probably not appropriate, the statement conveys the correct idea that $\Delta_r G^o$ tells us whether or not a given reaction will really run spontaneously. (You can probably write and balance a large number of reactions, but just because you can write and balance a reaction is no guarantee that it will run.)

We see from Equation 6 that the "driving force" of a chemical reaction has two components:

$\Delta H$ is the drive toward stability. When $\Delta H < 0$ the products are more stable than the reactants (and vice versa).

$\Delta S$ is the drive toward disorder. When $\Delta S > 0$ the products are more disordered than the reactants.

(The negative sign in front of the $T\Delta S$ shows that a positive $\Delta S$ makes a negative contribution to $\Delta G$ which tends to drive the reaction in the forward direction.)

Note that increasing $T$ increases the influence of $\Delta S$ on the reaction "driving force."

For a chemical reaction $\Delta H$ and $\Delta S$ are independent of each other. that is, you can not calculate one from the other. You can have situations where both are positive, both are negative, or one is positive and the other negative. Notice that if $\Delta H$ and $\Delta S$ have the same sign they are working against each other. You can make the entropy win by increasing the temperature or you can make the enthalpy win by decreasing the temperature.

We will show later that $\Delta_r G^o$ is related to the equilibrium constant for the reaction ( as you might expect).

22nd April, 2025

nPt

Solution to Test

(1a) $U_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$ ✓

$\Delta p = 100kpa - 150\,kpa$ ✓

$\Delta T = -0.625\,K$ ✓

$U_{JT} = \frac{-0.625}{-150kpa} = 0.0125\,K/kpa$ ✓

(1b) Heat, pressure, volume

(2) $\Delta u = q + w$

$du = dq - pdV$

$P_1 = 15.2\times10^5,\ P_2 = 10.1\times10^5$

$du = -pdV$

$\Delta u = -p(V_2 - V_1)$

$V = \frac{nRT}{P} = \frac{0.8\times 8.314\times 300}{15.2\times10^5} = 1.312\times10^{-3}\,m^3$

$\gamma = \frac{C_v + R}{C_v} = \frac{12.47 + 8.314}{12.47} = 1.67$

$V_2 = \left(\frac{P_1 V_1}{P_2}\right)^{1/\gamma} = \left(\frac{15.2\times10^5 \times 1.312\times10^{-3}}{10.1\times10^5}\right)^{1/1.67} = 0.00165\,m^3$

$$W = \frac{-\text{const}}{-\gamma+1}\left(\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}}\right)$$

$$W = \frac{15.2\times10^5 \times (1.312\times10^{-3})^{1.667}}{-1.667+1}\left(\frac{1}{(0.00168)^{0.667}} - \frac{1}{(0.001312)^{0.667}}\right)$$

$$= -456.107\,J$$

③ $du = Tds - pdv$

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$$

$$T = \left(\frac{\partial u}{\partial s}\right)_v$$

$$P = -\left(\frac{\partial u}{\partial V}\right)_s$$

# CHM 304

28/04/2025

Third law of Thermodynamics — Entropy at absolute zero temperature and total entropy of phase changes.

Content.

1. Application of thermodynamics concepts to mixtures and solutions
2. Entropy, enthalpy, and free energy of mixing
3. Open system and chemical potential
4. Chemical potential of ideal gas mixture or solution
5. Fugacity function
6. Partial molar quantities — Gibbs-Duhem equation
7. Phase rule and phase diagrams
8. Ideal binary mixtures - Raoult's and Henry's laws
9. Solubility and pressure
10. Solubility and temperature
11. Solutions of involatile solutes — The colligative properties.
12. Colligative properties of electrolytes.

# CHM 304

## Introduction.

The study of solutions is of great importance because many interesting and useful chemical and biological processes occur in liquid solutions. Generally, a solution is defined as a homogeneous mixture of two or more components that form a single phase. Most solutions are liquids, although gas solutions (e.g., air) and solid solutions (e.g., solder) also exist.

This study is on the thermodynamics of ideal and nonideal solutions of nonelectrolytes — solutions that do not contain ionic species — and the colligative properties of these solutions.

## Concentration Units

Any quantitative study of solutions requires that we know the amount of solute dissolved in a solvent or the concentration of the solution. Chemists employ several different concentration units. The use of the solution generally determines how we express its concentration. Examples of concentration units include percent by weight, mole fraction, molarity, and molality.

(i) Percent by Weight

The percent by weight (also called percent by mass) of a solute in a solution is defined as

$$\text{percent by weight} = \frac{\text{Weight of solute}}{\text{Weight of solute + Weight of solvent}} \times 100\%$$

$$= \frac{\text{Weight of solute}}{\text{Weight of solution}} \times 100\% \quad \text{—— (1)}$$

(ii) Mole fraction ($x$)

We define the mole fraction of a component i of a solution, $x_i$, as

$$x_i = \frac{\text{number of moles of component i}}{\text{number of moles of all components}}$$

$$= \frac{n_i}{\sum_i n_i} \quad \text{—— (2)}$$

The mole fraction has no units.

(iii) Molarity (M)

Molarity is defined as the number of moles of solute dissolved in 1 liter of solution, that is

$$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{liter of solution.}} \quad \text{—— (3)}$$

Thus, molarity has the units moles per liter (mol $L^{-1}$)
By convention, we use square brackets [ ] ~~for~~ represent molarity.

(iv) Molality (m)

Molality is defined as the number of moles of solute dissolved in 1 kg (1000g) of solvent; that is,

$$\text{Molality} = \frac{\text{number of moles of solute}}{\text{Mass of solvent in kg.}} \quad \text{———} (4)$$

Thus, molality has the units of moles per kg of solvent (mol $kg^{-1}$).

## Ideal solution

In ideal solutions, volumes are additive

(i) Intermolecular interactions are the same for all molecules $(\Delta_{mix} H^0)_{P,T} = 0$

(ii) Molecules have a finite volume independent of composition $(\Delta_{mix} V)_{P,T} = 0$

(iii) The solvent follows Raoult's law and the solute follows Henry's law.

(iv) The activity coefficient for all species is unity, that is, $\gamma = 1$.

(v) All mixtures are miscible (mix at all concentration) for all temperatures.

(vi) Mixing is driven only by a positive entropy change upon mixing. $\Delta_{mix} S^{\circ} > 0$

In general, solutions in the liquid phase are non-ideal. Non-ideal solutions are called real solutions.

## Partial Molar Quantities

In discussing the properties of any solution, we cannot employ molar quantities; instead we use partial molar quantities.

Unlike ideal solutions, for most real solutions volumes are not additive. That is, adding 50ml of one liquid to 50ml of another does not lead to a mixture of 100ml final volume. To account for this, we introduce the concept of partial molar volume.

The partial molar volume is the change in volume upon addition of component 2 to component 1, holding all other variables – that is, P, T and moles of 1 – constant.

For example, at 298K, the molar volumes of:

water = 0.018 L

ethanol = 0.058 L.

If we mix half a mole of each liquid, we might expect the combined volume to be 0.038L, i.e

$$\frac{0.018\,L}{2} + \frac{0.058\,L}{2} = 0.038\,L$$

Instead, we find the volume to be only 0.036L. The shrinkage of the volume is the result of unequal intermolecular interaction between unlike molecules. Because the forces of attraction between water and ethanol molecules are greater than those between water molecules and between ethanol molecules, the total volume is less than sum of the individual volumes.

If the intermolecular forces are weaker, then expansion will occur and the final volume will be greater than the sum of the individual volumes.

Only if the interaction between like and unlike molecules are the same will volume be additive. If the final volume is equal to the sum of the separate volumes, the solution is called an ideal solution.

At constant temperature and pressure, the volume of a solution is a function of the number of moles of different substances present; that is,

$$V = V(n_1, n_2, \ldots)$$

The total change in volume for infinitesimal changes in molar composition of a binary mixture of 1 and 2 is given as

$$dV = \left(\frac{\partial V}{\partial n_1}\right)_{P,T,n_2} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{P,T,n_1} dn_2$$

$$= \bar{V}_1 dn_1 + \bar{V}_2 dn_2 \qquad \text{——— (5)}$$

Where $\bar{V}_1$ and $\bar{V}_2$ are the partial molar volumes of component 1 and 2. The partial molar volume $\bar{V}_1$, for example, tells us the rate of change in volume with number of moles of component 1, at constant T, P, and Component 2. The quantity $\bar{V}_2$ can be similarly interpreted.

Equation (5) can be integrated to give

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 \quad \text{——— (6)}$$

This equation enables us to calculate the volume of the solution by summing the products of the number of moles and the partial molar volumes of each component.

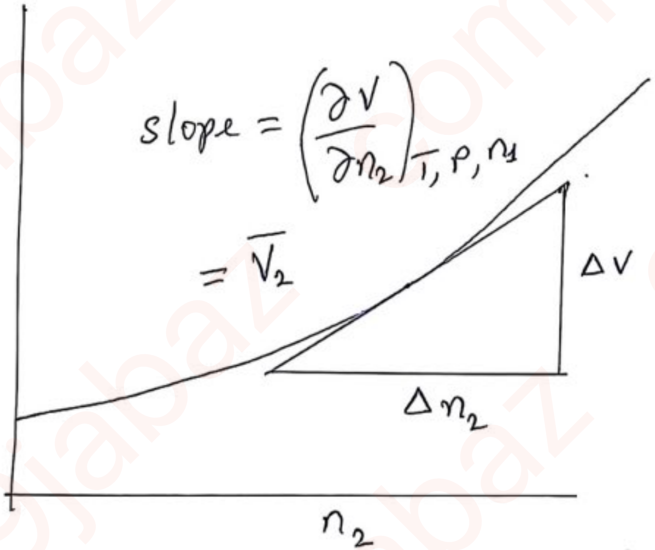


Fig 1. Determination of partial molar volume.

Figure 1 suggests a way of measuring partial molar volumes. Consider a solution composed of substances 1 and 2. To measure $\bar{V}_2$, we prepare a series of solutions at certain T, and P, all of which contain a fixed number of moles of component 1 (i.e, $n_1$ is fixed) but different amounts of $n_2$. When we plot the measured volume, V, of the solution against $n_2$, the slope of the curve at a particular composition of 2 gives $\bar{V}_2$ for that composition. Once $\bar{V}_2$ has been measured, $\bar{V}_1$ at the same composition can be calculated using equation 6:

$$\bar{V}_1 = \frac{V - n_2 \bar{V}_2}{n_1}.$$

Figure 2 shows the partial molar volume of ethanol-water solution. Note that whenever the partial molar volume of one component rises, that of the other component falls. This relationship is a characteristic of all partial molar quantities.

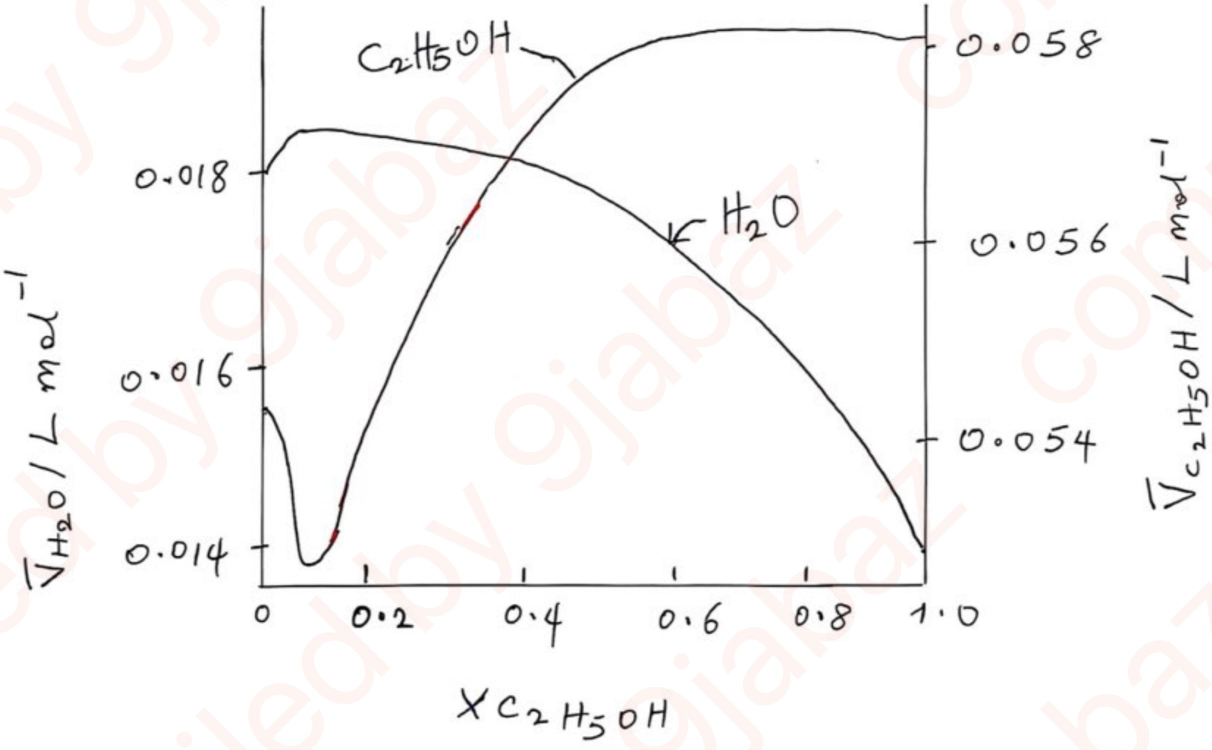


Fig. 2. The partial molar volumes of water and ethanol as a function of the mole fraction of ethanol.

# Partial Molar Gibbs Energy

Partial molar quantities permit us to express the total extensive properties, such as volume, energy, enthalpy, and Gibbs energy, of a solution of any composition.

The partial molar Gibbs energy of the ith component in solution $\bar{G}_i$ is given by

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j} \quad \text{———} \quad (7)$$

Where $n_j$ represents the number of moles of all other components present. Again we can think of $\bar{G}_i$ as the coefficient that gives the increase in the Gibbs energy of the solution upon the addition of 1 mole of component i at constant temperature and pressure to a large amount of solution of specified concentration.

Partial molar Gibbs energy is also called the chemical potential ($\mu$), so we can write

$$\bar{G}_i = \mu_i \quad \text{———} \quad (8)$$

## The Gibbs – Duhem Equation.

The chemical potentials of two components in a binary solution are not independent. This is very important because it allows the chemical potential of a nonvolatile solute such as sucrose in a volatile solvent such as water to be determined.

The differential form of the Gibbs energy is given by

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \text{ ——— } 9$$

where S is entropy.

For a binary solution at constant T and P, this equation reduces to

$$dG = \mu_1 dn_1 + \mu_2 dn_2 \text{ ——— } 10$$

Imagine starting with an infinitesimally small amount of a solution at constant T and P. The amount is gradually increased at constant composition. Because of this restriction, the chemical potentials are unchanged as the size of the system is changed. Therefore, the $\mu_i$ can be taken out of the integral.

$$\int_0^G dG = \mu_1 \int_0^{n_1} dn_1 + \mu_2 \int_0^{n_2} dn_2 \quad \text{or}$$

$$G = \mu_1 n_1 + \mu_2 n_2 \text{ ——— } 1.0b$$

The total differential of equation is

$$dG = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 \text{ ——— } 11$$

Equation 11 differ from equation 10 because, in general, we have to take the changes of the composition of the solution into account. Therefore $\mu_1$ and $\mu_2$ must be regarded as variables.

Equating the expression for dG in equation 10 and 11 gives the Gibbs - Duhem equation for a binary solution, i.e,

$$\mu_1 dn_1 + \mu_2 dn_2 = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2$$

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad \text{———} \quad 12$$

or

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

This equation states ~~that~~ the chemical potentials in a binary solution are not independent. Therefore,

If the change in the chemical potential of the first component is $d\mu_1$, the change of the chemical potential of the second component is given by

$$d\mu_2 = \frac{n_1 d\mu_1}{n_2} \quad \text{———} \quad 13$$

## Thermodynamics of Mixing.

The formation of solutions is generally governed by the principles of thermodynamics. Equation (106) gives the dependence of the Gibbs energy of a system on its composition, The spontaneous mixing of gases is accompanied by a change in composition; consequently, the systems's Gibbs energy decreases. The expression for the molar Gibbs energy of an ideal gas is

$$\bar{G} = \bar{G}^\circ + RT\ln\frac{P}{1\,\text{bar}}$$

In a mixture of ideal gases, the chemical potential of the ith component is given by

$$\mu_i = \mu_i^\circ + RT\ln\frac{P_i}{1\,\text{bar}} \quad \text{———}(14)$$

where $P_i$ is the partial pressure of component $i$ in the mixture and $\mu_i^\circ$ is the standard chemical potential of component $i$ when its partial pressure is 1 bar.

Consider the mixing $n_1$ moles of gas 1 at temperature $T$ and pressure $P$ with $n_2$ moles of gas 2 at the same $T$ and $P$. Before mixing, the total Gibbs energy of the system is given by equation 9, where chemical potentials are the same as molar Gibbs energies,

$$G = n_1\bar{G}_1 + n_2\bar{G}_2 = n_1\mu_1 + n_2\mu_2$$

$$G_{\text{initial}} = n_1(\mu_1^\circ + RT\ln P) + n_2(\mu_2^\circ + RT\ln P)$$

(For simplicity, we omit the term "1 bar". Note that the resulting P values are dimensionless.)

After mixing, the gases exert partial pressures $P_1$ and $P_2$, where $P_1 + P_2 = P$, and the Gibbs energy is

$$G_{\text{final}} = n_1(\mu_1^\circ + RT\ln P_1) + n_2(\mu_2^\circ + RT\ln P_2)$$

Note that $P_1 + P_2 = P$ only if there is no change in volume as a result of mixing: that is, $\Delta_{\text{mix}}V = 0$. This condition holds for ideal solutions.

The Gibbs energy of mixing, $\Delta_{mix}G$, is given by

$$\begin{aligned}\Delta_{mix}G &= G_{final} - G_{initial} \\ &= n_1RT\ln\frac{P_1}{P} + n_2RT\ln\frac{P_2}{P} \\ &= n_1RT\ln x_1 + n_2RT\ln x_2\end{aligned}$$

where $P_1 = x_1P$ and $P_2 = x_2P$ and $x_1$ and $x_2$ are the mole fractions of 1 and 2, respectively. (The standard chemical potential, $\mu^\circ$ is the same in the pure state and in the mixture).

Further, from the relations

$$x_1 = \frac{n_1}{n_1+n_2} = \frac{n_1}{n}, \text{ and}$$

$$x_2 = \frac{n_2}{n_1+n_2} = \frac{n_2}{n}$$

where $n$ is the total number of moles, we have

$$\Delta_{mix}G = nRT(x_1\ln x_1 + x_2\ln x_2) \text{ ——— } (15)$$

Because both $x_1$ and $x_2$ are less than unity, $\ln x_1$ and $\ln x_2$ are negative quantities, and hence so is $\Delta_{mix}G$. This result is consistent with our expectation that the mixing of gases is a spontaneous process at constant $T$ and $P$.

Now we can calculate other thermodynamic quantities of mixing.

From equation (16), we see that at constant pressure

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \text{——— (16)}$$

Thus, the entropy of mixing is obtained by differentiating equation (15) with respect to temperature at constant pressure.

$$\left(\frac{\partial \Delta_{mix} G}{\partial T}\right)_p = nR(x_1 \ln x_1 + x_2 \ln x_2)$$

$$= -\Delta_{mix} S$$

$$\Delta_{mix} S = -nR(x_1 \ln x_1 + x_2 \ln x_2) \qquad \text{——— (17)}$$

The minus sign in equation (12) makes $\Delta_{mix} S$ a positive quantity, in accord with a spontaneous process.

The enthalpy of mixing is given by

$$\Delta_{mix} H = \Delta_{mix} G + T\Delta_{mix} S$$

$$= 0$$

This result is not surprising, because molecules of ideal gases do not interact with one another so no heat is absorbed or produced as a result of mixing.

Example 1.

Calculate the Gibbs energy and entropy of mixing 1.6 moles of argon at 1 atm and 25°C with 2.6 moles of nitrogen at 1 atm and 25°C. Assume ideal behaviour.

Solution.

The mole fractions of argon and nitrogen are

$$x_{Ar} = \frac{1.6}{1.6 + 2.6} = 0.38$$

$$x_{N_2} = \frac{2.6}{1.6 + 2.6} = 0.62$$

From equation (11)

$$\Delta_{mix} G = nRT(x_1 \ln x_1 + x_2 \ln x_2)$$

$$= (4.2\,\text{mol})(8.314\,\text{J K}^{-1}\text{mol}^{-1})(298\,\text{K})\,[(0.38)\ln 0.38 + (0.62)\ln 0.62]$$

$$= -6.9\,\text{kJ}$$

Because $\Delta_{mix} S = \Delta_{mix} G/T$, we write

$$\Delta_{mix} S = \frac{-6.9 \times 10^3\,\text{J}}{298\,\text{K}}$$

$$= 23\,\text{J K}^{-1}.$$

Comment

In this example, the gases are at the same temperature and pressure when they are mixed. If the initial pressures of the gases differ, then there will be two contributions to $\Delta_{mix} G$: the mixing itself and the changes in pressure.

# Binary Mixture of Volatile Liquids

The results obtained for mixtures of gases also apply to ideal liquid solutions. We shall consider a solution containing two volatile liquids, that is, liquids with easily measurable vapour pressures. Let us start with a liquid in equilibrium with its vapour in a closed container. Because the the system is at equilibrium, the chemical potentials of the liquid phase and the vapour phase must be the same, that is,

$$\mu^*(l) = \mu^*(g)$$

Where the asterisk denotes a pure component. Further, from the expression for $\mu^*(g)$ for an ideal gas, i.e,

$$\mu_i = \mu_i^\circ + RT\ln\frac{P_i}{1\,\text{bar}} \quad \text{———— (14)}$$

We can write

$$\mu^*(l) = \mu^*(g) = \mu^\circ(g) + RT\ln\frac{P^*}{1\,\text{bar}} \quad \text{———— (18)}$$

Where $\mu^\circ(g)$ is the standard chemical potential at $P^* = 1$ bar. For a two-component solution at equilibrium with its vapour, the chemical potential of each component is still the same in the two phases. Thus, for component 1 we write

$$\mu(l) = \mu(g) = \mu_1^\circ(g) + RT\ln\frac{P_1}{1\,\text{bar}} \quad \text{———— (19)}$$

Where $P_1$ is the partial pressure.

Because $\mu^\circ(g) = \mu_1^\circ(g)$, we can combine the previous two equations to get

$$\mu(l) = \mu_1^{o}(g) + RT\ln\frac{p_1}{1\,\text{bar}}$$

$$= \mu_1^{*}(l) - RT\ln\frac{p_1^{*}}{1\,\text{bar}} + RT\ln\frac{p_1}{1\,\text{bar}}$$

$$= \mu_1^{*}(l) + RT\ln\frac{p_1}{p_1^{*}} \quad \text{——} \quad (20)$$

Thus, the chemical potential of component 1 in solution is expressed in terms of the chemical potential of the liquid in the pure state and the vapour pressures of the liquid in solution and in the pure state.

## Raoult's Law

The french chemist François Marie Raoult's (1830 - 1901) found that for some solutions, the ratio of $p_1/p_1^*$ in equation (15) is equal to the mole fraction of component 1, that is,

$$\frac{p_1}{p_1^{*}} = x_1$$

or

$$p_1 = x_1 p_1^{*} \quad \text{——} \quad (21)$$

Equation 21 is known as Raoult's law.

Raoult's law states that the vapour pressure of a component of a solution is equal to the product of its mole fraction and the vapour pressure of the pure liquid.

Substituting equation (21) into equation (20), we obtain

$$\mu_1(l) = \mu_1^*(l) + RT\ln x_1 \quad \text{——} (22)$$

In a pure liquid

$x_1 = 1$ and $\ln x_1 = 0$

Therefore, equation (22) becomes

$$\mu_1(l) = \mu_1^*(l)$$

Solutions that obey Raoult's law are called ideal solutions.

An example of a near ideal solution is the benzene – toluene system.

Benzene

Toluene

The benzene – toluene system approximates ideal solution because benzene and toluene molecules have similar shapes and electronic structures.

Figure 3 shows a plot of the vapour pressure versus the mole fraction of benzene.

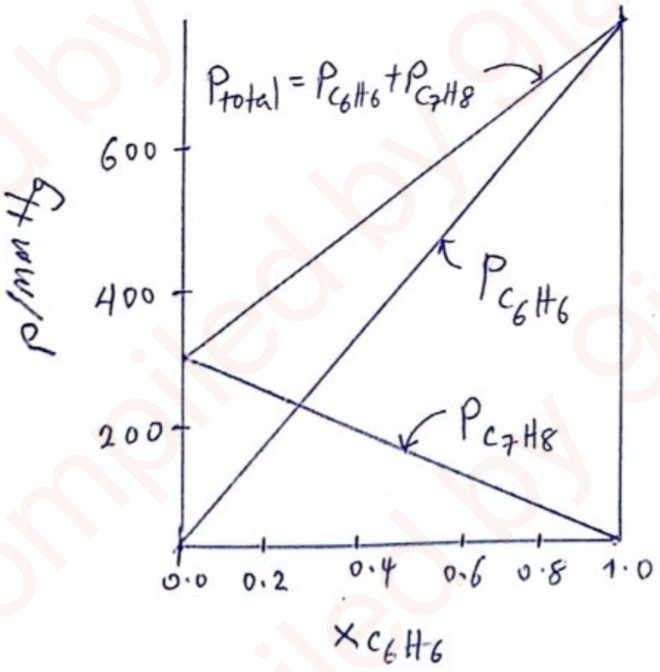


Fig. 3: Total vapour pressure of the benzene – toluene mixture as a function of the benzene mole fraction at 80.1°C.

## Example 2

Liquids A and B form an ideal solution. At 45°C, The vapour pressures of pure A and pure B are 66 torr and 88 torr, respectively. Calculate the composition of the vapour in equilibrium with a solution containing 36 mole percent A at this temperature.

## Solution:

Because $x_A = 0.36$

$$x_B = 1 - 0.36 = 0.64$$

According to Raoult's law

$$P_A = x_A P_A^* = 0.36 \times 66 \text{ torr} = 23.8 \text{ torr}$$

$$P_B = x_B P_B^* = 0.64 \times 88 \text{ torr} = 56.3 \text{ torr}$$

The total vapour pressure $P_T$, is given by

$$P_T = P_A + P_B = 23.8 \text{ torr} + 56.3 \text{ torr} = 80.1 \text{ torr}$$

Finally, The mole fraction of A and B in the vapour phase, $x_A^v$ and $x_B^v$, are given by

$$x_A^v = \frac{P_A}{P_T} = \frac{23.8 \text{ torr}}{80.1 \text{ torr}} = 0.30$$

and

$$x_B^v = \frac{P_B}{P_T} = \frac{56.3 \text{ torr}}{80.1 \text{ torr}} = 0.70$$

## Example 3

An ideal solution is made from 5.00 mol of benzene and 3.25 mole of toluene. Calculate $\Delta G_{mixing}$ and

$\Delta S_{mixing}$ at 298 K and 1 bar pressure. Is mixing a spontaneous process?

Solution.

The mole fractions of the components in the solution are

$$x_{benzene} = \frac{5.00}{5.00+3.25} = \frac{5.00}{8.25} = 0.606$$

$$x_{toluene} = \frac{3.25}{8.25} = 0.394$$

According to equation (11),

$$\Delta G_{mixing} = nRT \sum_i x_i \ln x_i$$

For a two-component solution

$$\Delta G_{mix} = nRT(x_1 \ln x_1 + x_2 \ln x_2)$$

If $x_{benzene} = x_1$, and

$x_{toluene} = x_2$, then

$$\Delta G_{mix} = 8.25 mol \times 8.314 J mol^{-1} K^{-1} \times 298 K \times (0.606 \ln 0.606 + 0.394 \ln 0.394)$$

$$= -13.7 \times 10^3 J$$

$$\Delta S_{mix} = -nR(x_1 \ln x_1 + x_2 \ln x_2)$$

$$= -8.25 mol \times 8.314 J mol^{-1} K^{-1} \times (0.606 \ln 0.606 + 0.394 \ln 0.394)$$

$$= 46.0 JK^{-1}$$

Mixing is spontaneous because $\Delta G_{mix} < 0$ for an ideal solution

NB: If two liquids are miscible, it is always true that $\Delta G_{mix} < 0$.

## Deviations from Raoult's law

1. positive deviation.

Example: Carbon disulfide - acetone system ($CS_2-CH_3COCH_3$)

Most solutions do no behave ideally. The positive deviation corresponds to the case in which the intermolecular forces between unlike molecules are weaker than those between like molecules, and there is a greater tendency for these molecules to leave the solution than in the case of an ideal solution. Consequently, the vapour pressure of the solution is greater than the sum of the vapour pressure for an ideal solution.

2. negative deviation

Example; Chloroform - acetone ($CHCl_3-CH_3COCH_3$) system.

Just the opposite of positive deviation holds for a negative deviation from Raoult's law. In this case, unlike molecules attract each other more strongly than they do their own kind, and the vapour pressure of the solution is less than the sum of the vapour pressures from an ideal solution.

# Henry's Law

When one solution component is present in excess (this component is called the solvent), it's vapour pressure is quite accurately described by equation (21). In contrast, the vapour pressure of the component present in small amount (this component is called the solute) does not vary with the composition of the solution, as predicted by equation (21). Still, the vapour pressure of the solute varies with concentration in a linear manner:

$$P_2 = Kx_2 \text{ ——————— } (23)$$

Equation (23) is known as Henry's law (after the English chemist William Henry, 1775-1836), where K, the Henry's law constant, has units of pressure.

Henry's law relates the mole fraction of the solute to its partial (vapour) pressure.

Alternatively, Henry's law can be expressed as

$$P_2 = K'm \text{ ——————— } (24)$$

where m is the molality of the solution and the constant K' now has the units atm mol$^{-1}$ kg of the solvent.

Henry's law is normally associated with solutions of gases in liquids, although it is equally applicable to solutions containing nongaseous volatile solutes.

It has great practical importance in chemical and biological systems:

(i) The effervescence observed when a drink or champagne bottle is opened is a demonstration of the decrease in gas — mostly $CO_2$ — solubility as its partial pressure is lowered.

(ii) The emboli (gas bubbles in the bloodstream) suffered by deep-sea divers who rise to the surface too rapidly also illustrate Henry's law.

## Deviations from Henry's law

There are several types of deviations from Henry's law:

(i) The law holds only for dilute solutions

(ii) If the dissolved gas interacts chemically with the solvent, then the solubility can be greatly enhanced. Gases such as $CO_2$, $H_2S$, $NH_3$, and HCl all have high solubilities in water because they react with the solvent

(iii) The third type of deviation is illustrated by the dissolution of oxygen in blood. Normally, oxygen is only sparingly soluble in water, but its solubility increases dramatically if the solution contains hemoglobin or myoglobin.

## Example 4

Calculate the molal solubility of carbon dioxide in water at 298K and a $CO_2$ pressure of

$3.3 \times 10^{-4}$ atm, which corresponds to the partial pressure of $CO_2$ in air. The Henry's law constant, K, for $CO_2$ is given as $1.24 \times 10^{6}$ torr ( $K'$ is 29.3 atm mol$^{-1}$ kg of water.

**Solution**

The mole fraction of solute ( $CO_2$ ) is given as:

$$X_{CO_2} = \frac{P_{CO_2}}{K}$$

Because the number of moles of $CO_2$ dissolved in 1000g of water is small, we can approximate the mole fraction as follows:

$$X_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{H_2O}} = \frac{n_{CO_2}}{n_{H_2O}}$$

So that

$$n_{CO_2} = \frac{P_{CO_2} n_{H_2O}}{K}$$

Finally,

$$n_{CO_2} = (3.3 \times 10^{-4} \times 760)\text{torr} \times \frac{1000g}{18.01 g mol^{-1}} \times \frac{1}{1.24 \times 10^{6} \text{torr}}$$

$$= 1.12 \times 10^{-5} \text{mol}.$$

NB: 1 atm = 760 torr.

Because this is the number of moles of $CO_2$ in 1000g or 1kg of $H_2O$, the molality is $1.12 \times 10^{-5}$ mol (kg $H_2O$)$^{-1}$.

Alternatively,

We can use equation (24) and proceed as follows:

$$m = \frac{P_{CO_2}}{K'}$$

$$= \frac{3.3 \times 10^{-4}\,\text{atm}}{29.3\,\text{atm}\,\text{mol}^{-1}\,\text{kg}\,H_2O}$$

$$= 1.12 \times 10^{-5}\,\text{mol}\,(\text{kg}\,H_2O)^{-1}$$

Example 5.

The average human with a 70 kg has a blood volume of 5.00 L. The Henry's law constant for the solubility of $N_2$ in $H_2O$ is $9.04 \times 10^4$ bar at 298 K. Assume that this is also the value of the Henry's law constant for blood and that the density of blood is $1.00\,\text{kg}\,\text{L}^{-1}$.

Calculate the number of moles of nitrogen absorbed in this amount of blood in air of composition 80.% $N_2$ at sea level, where the pressure is 1 bar, and at pressure of 50 bar.

SOLUTION

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

$$\text{mass} = \text{Density} \times \text{volume}$$

$$\text{Mass} = 1.00\,\text{kg}\,L^{-1} \times 5.00\,L$$
$$= 5.0\ \text{kg} = 5.0 \times 10^3\,g.$$

Density of blood = Density of $H_2O$

∴ Mass of blood = mass of $H_2O$.

Because the number of moles of $N_2$ dissolved in 1000g of blood ($\equiv H_2O$) is small, we can approximate the mole fraction as follows:

$$x_{N_2} = \frac{P_{N_2}}{K}$$

$$= \frac{n_{N_2}}{n_{N_2} + n_{H_2O}} = \frac{n_{N_2}}{n_{H_2O}} = \frac{P_{N_2}}{K}$$

$$\therefore n_{N_2} = n_{H_2O}\frac{P_{N_2}}{K}$$

(a) $$n_{H_2O} = \frac{\text{mass of } H_2O}{\text{Molar mass of } H_2O}$$

$$MM_{H_2O} = 18.02\,g\,mol$$

$$\therefore n_{N_2} = \frac{5.0 \times 10^3\,g}{18.02\,g\,mol^{-1}} \times \frac{0.80\,bar}{9.04 \times 10^4\,bar}.$$

$$= 2.5 \times 10^{-3}\,mol$$ at 1bar total pressure.

NB: $P_{N_2}$ is taken as 0.80 bar because the air is said to be composed of 80% of $N_2$ at sea level, where the pressure is 1bar.

At 50 bar, $n_{N_2} = 50 \times 25 \times 10^{-3}$ mol.

$= 0.13$ mol.

## Real Solutions

As pointed out earlier, most solutions do not behave ideally. One problem that immediately arises in dealing with nonideal solutions is how to write the chemical potentials for the solvent and solute components.

### The solvent component

The chemical potential of the solvent in an ideal solution is given as

$$\mu(l) = \mu_1^*(l) + RT \ln x_1 \quad \text{———— (22)}$$

where $x_1 = P_1/P_1^*$ and $P_1^*$ is the equilibrium vapour pressure of pure component 1 at T. The standard state is the pure liquid and is attained when $x_1 = 1$.

For nonideal solution, we write

$$\mu_1(l) = \mu_1^*(l) + RT \ln a_1 \quad \text{———— (25)}$$

where $a_1$ is the activity of the solvent. Nonideality is the consequence of unequal intermolecular forces between solvent-solvent and solvent-solute molecules. Therefore, the extent of nonideality depends on the composition of solution, and the activity of the solvent plays the role of "effective" concentration.

The solvent's activity can be expressed in terms of vapour pressure as

$$a_1 = \frac{P_1}{P_1^*} \text{ ——— } (26)$$

Where $P_1$ is the partial ~~vapour~~ vapour pressure of component 1 over the (nonideal) solution.

Activity is related to concentration (mole fraction) as follows:

$$a_1 = \gamma_1 x_1 \text{ ——— } (27)$$

where $\gamma_1$ is the activity coefficient.

Equation (25) can now be written as

$$\mu_1(l) = \mu_1^*(l) + RT\ln\gamma_1 + RT\ln x_1 \text{ —— } (28)$$

The value of $\gamma_1$ is a measure of the deviation from ideality.

In the limiting case, where $x_1 \to 1$, $\gamma_1 \to 1$ and activity and the mole fraction are identical. This condition also holds for an ideal solution at all concentrations.

## The solute component

In dilute, nonideal solutions in which there is no chemical interaction, the solvent obeys Raoult's law, and the solute obeys Henry's law. Such solutions are sometimes called "ideal dilute solutions". If the solution were ideal, the chemical potential of the solute is also given by Raoult's law.

$$\mu_2(l) = \mu_2^*(l) + RT\ln x_2$$

$$= \mu_2^*(l) + RT\ln \frac{P_2}{P_2^*}$$

In an ideal dilute solution, Henry's law applies. That is $P_2 = Kx_2$ that

$$\mu_2(l) = \mu_2^*(l) + RT\ln \frac{Kx_2}{P_2^*}$$

$$= \mu_2^*(l) + RT\ln \frac{K}{P_2^*} + RT\ln x_2$$

$$= \mu_2^\circ(l) + RT\ln x_2 \quad \text{------} \quad (28)$$

where $\mu_2^\circ(l) = \mu_2^*(l) + RT\ln(K/P_2^*)$.

Equation (28) holds only for dilute solutions.

For nonideal solutions in general (beyond the dilute solution limit) equation (28) is modified to

$$\mu_2(l) = \mu_2^\circ(l) + RT\ln a_2 \quad \text{------} \quad (29)$$

where $a_2$ is the activity of the solute.

As in the case of the solvent component, we have $a_2 = \gamma_2 x_2$, where $\gamma_2$ is the activity coefficient of the solute.

Here we have $a_2 \rightarrow x_2$ or $\gamma_2 \rightarrow 1$ as $x_2 \rightarrow 0$.

Henry's law is now given by

$$P_2 = K a_2 \quad \text{———} \quad (30)$$

Concentrations are usually expressed in molalities (or molarities) instead of mole fractions.

In molality, equation (28) takes the form

$$\mu_2(l) = \mu_2^{\circ}(l) + RT \ln \frac{m_2}{m^{\circ}} \quad \text{———} \quad (31)$$

Where $m^{\circ} = 1 \text{ mol kg}^{-1}$ so that the ratio $m_2/m^{\circ}$ is dimensionless.

For nonideal solutions, equation (31) is rewritten as

$$\mu_2(l) = \mu_2^{\circ}(l) + RT \ln a_2 \quad \text{———} \quad (32)$$

Where $a_2 = \gamma_2 (m_2/m^{\circ})$.

In the limiting case of $m_2 \rightarrow 0$, we have $a_2 \rightarrow m_2/m^{\circ}$ or $\gamma_2 \rightarrow 1$.

Example 7

Calculate the activity and activity coefficient for $CS_2$ at $x_{CS_2} = 0.3502$; given that $P_{CS_2} = 358.3$ torr and $P^{*}_{CS_2}$ (vapour pressure of pure $CS_2$) $= 512.3$ torr. Assume a Raoult's law standard state.

## solution

$$a_{CS_2} = \frac{P_{CS_2}}{P^*_{CS_2}} = \frac{358.3 \text{ torr}}{512.3 \text{ torr}} = 0.6994$$

$$\gamma_{CS_2} = \frac{a_{CS_2}}{x_{CS_2}} = \frac{0.6994}{0.3502} = 1.997.$$

## Colligative properties

Many solutions consist of nonvolatile solutes that have limited solubility in a volatile solvent. Examples are solutions of sucrose or sodium chloride in water. Important properties of these solutions, including boiling point elevation, freezing point depression and osmotic pressure are found to depend only on the solute concentration(i.e the number of solute molecules present) — not on the size or molar-mass of the molecules. These properties are called colligative, or collective, properties.

If the vapour pressure of the solvent follows Raoult's law, then

$$P_1 = P_1^* x_1$$

Because $x_1 = 1 - x_2$, in the presence of a nonvolatile solute, the equation above becomes

$$P_1 = (1 - x_2) P_1^*$$

Rearranging this equation gives

$$P_1^* - P_1 = \Delta P = x_2 P_1^* \quad \text{———} \quad (33)$$

where $\Delta p$, the decrease in vapour pressure from that of the pure solvent, is directly proportional to the mole fraction of the solute.

## Boiling-point Elevation

The boiling point of a solution is the temperature at which its vapour pressure is equal to the external pressure.

For a solution containing a nonvolatile solute, the boiling point elevation originates in the change in the chemical potential of the solvent due to the presence of the solute.

According to equation (22) earlier discussed; i.e

$$\mu_1(l) = \mu_1^*(l) + RT\ln x_1 \quad \text{———} \quad (22)$$

the chemical potential of the solvent in a solution is less than the chemical potential of the pure solvent by an amount equal to $RT\ln x_1$.

Fig 4 illustrates how this change affects the boiling point of the solution.

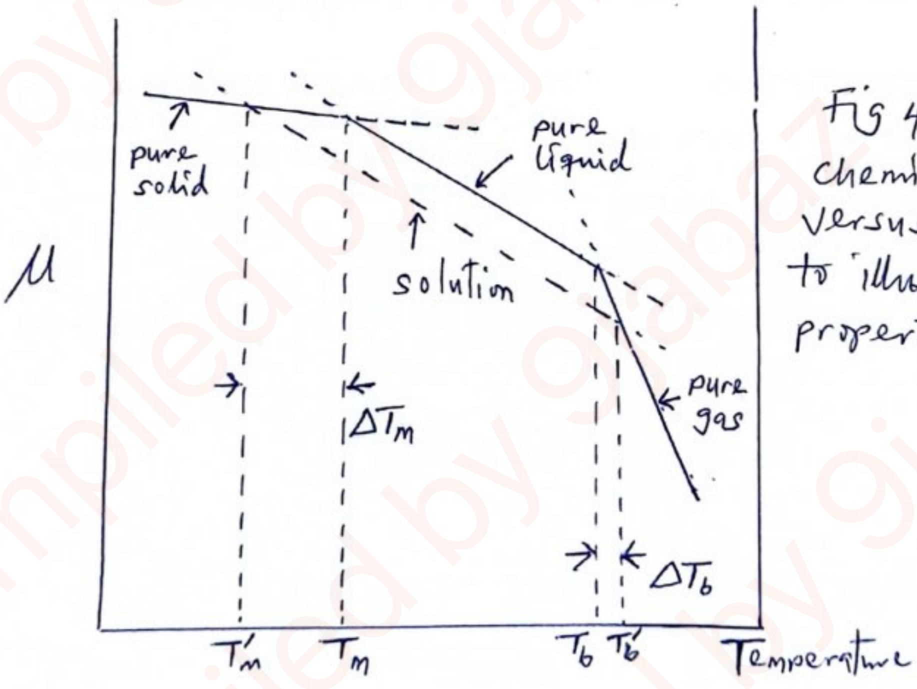


Fig 4: plot of chemical potentials versus temperature to illustrate colligative properties.

Because the solute is nonvolatile, it does not vapourise; therefore, the curve for the vapour phase is the same as that for the pure vapour. On the other hand, because the liquid contains a solute, the chemical potential of the solvent decreases. The points where the curve for the vapour intersects the curves for the liquid (pure and solution) correspond to the boiling points of the pure solvent and the solution, respectively. From the plot, we see that the boiling point of the solution ($T'_b$) is higher than that of the pure solvent ($T_b$).

At the boiling point the solvent vapour is in equilibrium with the solvent in solution, so that

$$\mu_1(g) = \mu_1(l) = \mu_1^*(l) + RT\ln x_1$$

or

$$\Delta\mu_1 = \mu_1(g) - \mu_1^*(l) = RT\ln x_1 \quad \text{———} \quad (34)$$

where $\Delta\mu_1$ is the Gibbs energy change associated with the evaporation of 1 mole of solvent from the solution at temperature, $T$, its boiling point.

Thus, we can write

$$\Delta\mu_1 = \Delta_{vap}\overline{G}.$$

Dividing equation (34) by $T$, we obtain

$$\frac{\Delta_{vap}\overline{G}}{T} = \frac{\mu_1(g) - \mu_1^*(l)}{T} = R\ln x_1$$

According to the Gibbs-Helmholtz equation; i.e

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_P = -\frac{\Delta H}{T^2} \quad \text{————} \quad (35)$$

we write

$$\frac{d(\Delta G/T)}{dT} = -\frac{\Delta H}{T^2} \quad (\text{at constant } p)$$

or

$$\frac{d(\Delta_{vap}\bar{G}/T)}{dT} = \frac{-\Delta_{vap}\bar{H}}{T^2} = R\frac{d(\ln x_1)}{dT}$$

where $\Delta_{vap}\bar{H}$ is the molar enthalpy of vaporization of the solvent from the solution.

Because the solution is dilute, $\Delta_{vap}\bar{H}$ is taken to be the same as the molar enthalpy of vaporization of the pure solvent.

Rearranging the last equation gives

$$d\ln x_1 = -\frac{\Delta_{vap}\bar{H}}{RT^2}dT \quad \text{———} \quad (36)$$

Integration of equation (36) between the limits $T_b'$ and $T_b$; and because the mole fraction of the solvent is $x_1$ at $T_b'$ and 1 at $T_b$, we write

$$\int_{\ln 1}^{\ln x_1} d\ln x_1 = \int_{T_b}^{T_b'} -\frac{\Delta_{vap}\bar{H}}{RT^2}dT$$

$$\ln x_1 = -\frac{\Delta_{vap}\bar{H}}{R}\left(\frac{1}{T_b'} - \frac{1}{T_b}\right)$$

$$= -\frac{\Delta_{vap}\bar{H}}{R}\left(\frac{T_b' - T_b}{T_b' T_b}\right)$$

$$= -\frac{\Delta_{vap}\bar{H}}{R}\frac{\Delta T}{T_b^2} \quad \text{———} \quad (37)$$

where $\Delta T = T_b' - T_b$.

To arrive at equation (37) two assumptions were made, both of which are based on the fact that $T'_b$ and $T_b$ differ only by a small amount (a few degrees).

(i) we assumed $\Delta_{vap}\bar{H}$ to be temperature independent

(ii) $T'_b \approx T_b$, so that $T'_b T_b \approx T_b^2$.

If we express the concentration in terms of the amount of solute present, we write

$$\ln x_1 = \ln(1-x_2) = -\frac{\Delta_{vap}\bar{H}}{R}\frac{\Delta T}{T_b^2}$$

where, by Maclaurin's series,

$$\ln(1-x_2) = -x_2 - \frac{x_2^2}{2} - \frac{x_2^3}{3}\cdots$$
$$\approx -x_2 \quad (x_2 << 1)$$

we now have

$$\Delta T = \frac{RT_b^2}{\Delta_{vap}\bar{H}}x_2.$$

To convert the mole fraction $x_2$ into a more practical concentration unit, such as molality $(m_2)$, we write

$$x_2 = \frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1} = \frac{n_2}{w_1/M_1} \qquad (n_1 >> n_2)$$

where $w_1$ is the mass of the solvent in kg and $M_1$ is the molar mass of the solvent in kgmol$^{-1}$, respectively.

NB: $\dfrac{n_2}{w_1/M_1} = \dfrac{n_2}{w_1}M_1$.

where $\frac{n_2}{w_1}$ gives the molality of the solution, $m_2$.

$\therefore x_2 = M_1 m_2$, and thus,

$$\Delta T = \frac{RT_b^2 M_1}{\Delta_{vap}\bar{H}} m_2 \quad \text{———} \quad (38)$$

Note that all the quantities in the first term on the right of equation (38) are constants for a given solvent, and so we have

$$K_b = \frac{RT_b^2 M_1}{\Delta_{vap}\bar{H}} \quad \text{———} \quad (39)$$

where $K_b$ is called the molal boiling-point-elevation constant. The units of $K_b$ are $K\,mol^{-1}\,kg$.

finally,

$$\Delta T = K_b m_2 \quad \text{———} \quad (40)$$

Figure 5 shows the phase diagrams of pure water and an aqueous solution. Upon the addition of non-volatile solute, the vapour pressure of the solution decreases at every temperature. Consequently, the boiling point of the solution at 1 atm will be greater than 373.15K.

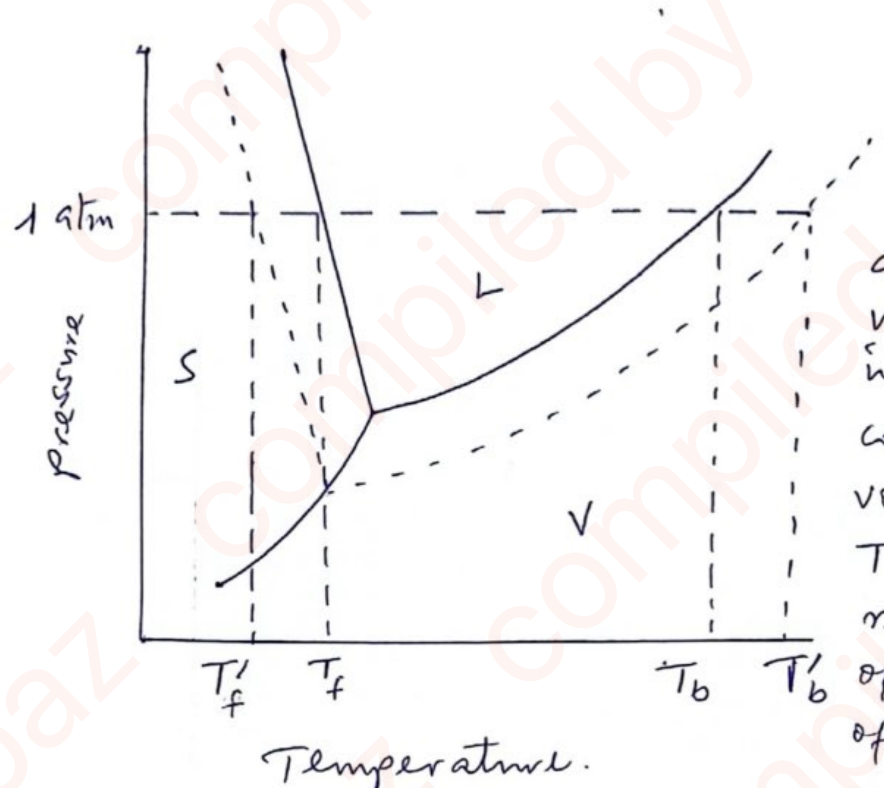


Fig 5: phase diagrams of pure water and of water in an aqueous solution containing a non volatile solid. $T'_f$, $T_f$, $T_b$ and $T'_b$ represent freezing point of solution, freezing point of solvent, boiling point of solvent and boiling point of solution, respectively.

## Freezing-point Depression

The thermodynamic analysis of freezing-point depression is similar to that of boiling point elevation. If we assume that when a solution freezes, the solid that separates from the solution contains only the solvent, then the curve for the chemical potential of the solid does not change (Fig. 4). Consequently, the solid curve for the solid and the dashed curve for the solvent in solution now intersect at a point ($T'_f$) below the freezing point of the pure solvent ($T_f$).

By following the same procedure as that for the boiling-point elevation, we can show that the drop in freezing-point, $\Delta T$, (i.e; $T_f - T'_f$) is

$$\Delta T = K_f m_2 \quad \text{———} (41)$$

where $K_f$ is the molal freezing-point-depression constant given by

$$K_f = \frac{RT_f^2 M_1}{\Delta_{fus}\bar{H}} \quad \text{———— (42)}$$

where $\Delta_{fus}\bar{H}$ is the enthalpy of fusion of the solvent.

Application of freezing-point depression phenomenon

The freezing point depression phenomenon has many examples in everyday life and in biological systems.

(i) Salts, such as sodium chloride ($NaCl$) and calcium chloride ($CaCl_2$) are used to melt ice on roads and sidewalks. Ice on winter roads and sidewalks melts readily when sprinkled with salt. This method of thawing depresses the freezing-point of water.

(ii) The organic compound ethylene glycol [$CH_2(OH)CH_2(OH)$] is the common automobile antifreeze. It is also employed to de-ice airplanes.

Example 8

For a solution of 45.20g of sucrose ($C_{12}H_{22}O_{11}$) in 316.0g of water, calculate (a) the boiling point and (b) the freezing point. $K_b$ and $K_f$ for water are 0.51 K mol⁻¹ kg and 1.86 K mol⁻¹ kg, respectively.

Solution

(a) The molality of the solution is given by

# Class Notes/Jottings With Questions

(i) Application of thermodynamic concept to mixture and solution

(ii) Entropy, Enthalpy and free energy of mixing

(iii) Open system and chemical potential

(iv) Chemical potential of ideal gas mixture or solution

(v) Fugacity function

(vi) Partial molar quantities – Gibbs-Duhem equation

(vii) Gibbs phase rule and phase Diagram

(viii) Ideal binary mixtures – Raoult's and Henry's laws.

(ix) Solubility and pressure

(x) Solubility and temperature

(xi) Solutions of involatile solutes – The Colligative properties

(xii) Colligative properties of electrolyte

# Some of Quantities Used

Percent by Weight ⇒

$$\frac{\text{Weight of Solute}}{\text{Weight of Solute} + \text{[illegible] solvent}} \times 100\%$$

$$= \frac{\text{Weight of Solute}}{\text{Weight of Solution}} \times 100\%$$

**Mole Fraction (x)** – Is defined by no of moles of

$$\frac{\text{no of moles of Component } i}{\text{no of moles of all Components}}$$

$$= \frac{n_i}{\Sigma_i n} \quad \ldots\ldots ②$$

⇒ The mole fraction has no unit.

**Molarity** – It expresses the amount of mole in 1L. It is the no of moles of solute dissolved in 1L of Solution.

$$M = \frac{\text{no of moles of Solute}}{\text{1 litre of solution}} \quad (\text{mol L}^{-1})$$

**Molality** – No of mole of Solute dissolved in 1kg (1000g) of Solvent.

$$\text{Molality} = \frac{\text{no of moles of Solute}}{\text{Mass of Solvent}} \quad (\text{mol kg}^{-1})$$

# Ideal Solution.

## Propoties

① Intemolecular Interactions are the same for all molecules
$(\Delta_{mix} H^{\circ})_{P,T} = 0$

② Molecules have finite Volume Independent of Composition.
$(\Delta_{mix} V)_{T,P} = 0$

③ The solvent follows Raoult's law & the ~~Solute~~ Solute follows Henry's law.

④ The activity coefficient for all Species is Unity
$\gamma = 1$

⑤ All mixtures are miscible i.e they mix at all Concentrations and temperature.

⑥ Mixing is driven by a positive entropy change upon mixing. $(\Delta_{mix} S^{\circ})_{T,P} > 0.$

However, In general Solution in the liquid phase are non-ideal. Non-Ideal solutions are called real Solution

## Partial Molar Quantities.

The partial molar Volume is the Change In Volume upon addition of component 2 to component 1 holding all other Variables i.e P, T and moles of 1 constant. Unlike ideal solutions, ~~Volumes are not additive~~ Real Solution Volumes are not ADDITIVE

$V = V(n_1, n_2)$

$$dV = \left(\frac{\partial V}{\partial n_1}\right)_{T, P, n_2} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{T, P, n_1} dn_2$$

Note: Const. T & const. P

$$dV = \bar{V}_1 dn_1 + \bar{V}_2 dn_2$$

$$\int_0 dV = \bar{V}_1 \int_0^{n_1} dn_1 + \bar{V}_2 \int_0^{n_2} dn_2$$

$$V = \bar{V}_1 n_1 + \bar{V}_2 n_2$$

$\bar{V}_2$ = Molar volume of 2

$$\boxed{\bar{V}_2 = \frac{V - \bar{V}_1 n_1}{n_2}}, \quad \boxed{\bar{V}_1 = \frac{V - \bar{V}_2 n_2}{n_1}}$$

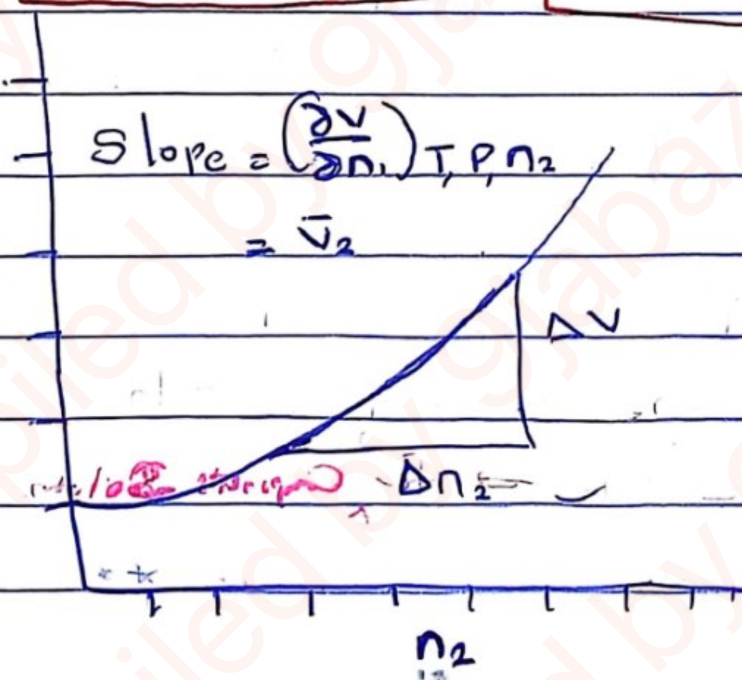


Fig 1

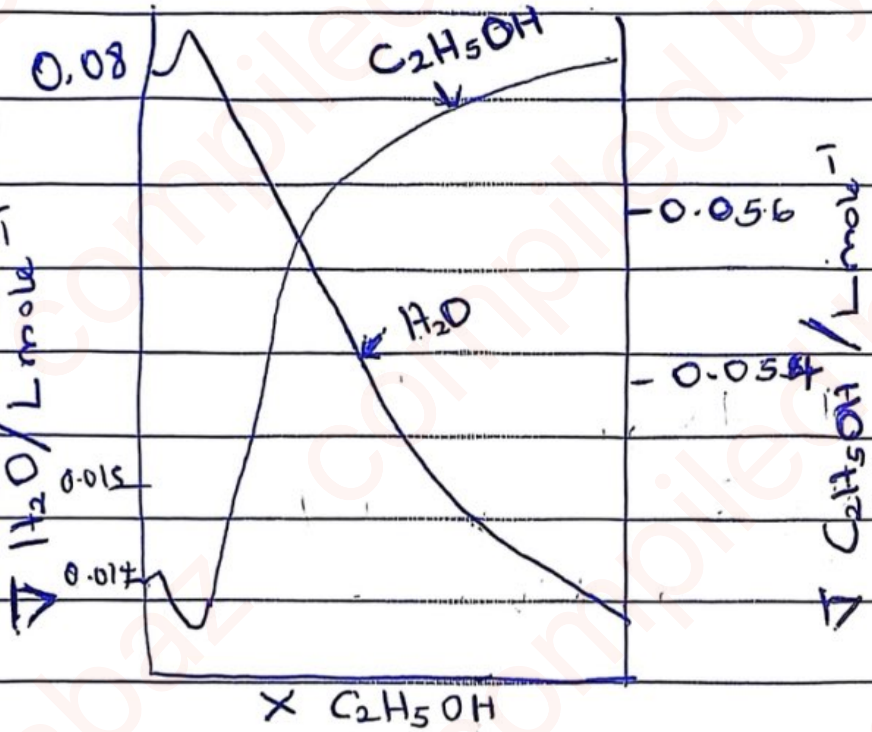


Fig 2:

## Partial Molar Gibb's Energy.

Partial molar quantities permit us to express the total extensive properties such as volume, energy, enthalpy & Gibbs energy.

i = Component will are considering

j = All other Components present

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,\,P,\,n_j}$$

i = Component will are considering

j = All other Components

### The Gibbs - Duhem Equation.

[$\mu$ = chemical potential]

$$dG = -SdT + Vdp + \Sigma_i \mu_i dn_i$$

$dG = \Sigma_i \mu_i dn_i \Rightarrow$ for 2 Components Solution

$dG = \mu_1 dn_1 + \mu_2 dn_2$

# Gibbs- Duhem Equation.

It simply the chemical potential in two binary solutions are not Independent.

$$dG = \mu_1 dn_1 + \mu_2 dn_2.$$

$$\int_0^G dG = \mu_1 \int_0^{n_1} dn_1 + \mu_2 \int_0^{n_2} dn_2$$

$\Rightarrow$ [If addition of the two is -ve It is Spontaneous]

$$G = \mu_1 n_1 + \mu_2 n_2 \ldots **$$

$$dG = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 \ldots **$$

$$\mu_1 \cancel{dn_1} + \mu_2 \cancel{dn_2} = \mu_1 \cancel{dn_1} + n_1 d\mu_1 + \mu_2 \cancel{dn_2} + n_2 d\mu_2$$

$$\boxed{\begin{aligned} n_1 d\mu_1 + n_2 d\mu_2 &= 0 \\ x_1 d\mu_1 + x_2 d\mu_2 &= 0. \end{aligned}} \Leftarrow \text{Gibbs - Duhem Equation.}$$

If the (chemical potential of the first component is $d\mu_1$

$$\therefore x_1 d\mu_1 = -x_2 d\mu_2.$$

## Thermodynamics of Mixing. $\Leftarrow$ (The one in large quantity = Solvent)

For a gaseous system,

$$\bar{G} = \bar{G}^* + RT \ln \frac{P^*}{1\,bar}$$

[$\bar{G}^*$ = Molar free mixing energy of the Solution]

In a mixture of ideal gases, the chemical potential of the ~~bright~~ i component is given.

$$\bar{G}_i = \mu_i$$

$$\mu_i = \mu_i^\circ + RT \ln \frac{P_i}{1\,\text{bar}}$$

Where $P_i$ = partial pressure of component "i" in the mixture.

$\mu_i^0$ = Standard chemical potential of component i when its standard partial pressure is <u>1 bar</u>.

Gaseous System

$$\mu_i = \mu_i \bar{G}_i + \mu_2 \bar{G}_2 = \bar{G}_i$$

~~The Standard~~ chemical

02|05|2025

$$\bar{G} = \bar{G}^\circ + RT \ln \frac{P}{1\,\text{bar}}$$

$$\bar{G}^\circ = \mu^0$$

Already contain

$$\boxed{\bar{G} = \mu_i^0 + RT \ln \frac{P}{1\,\text{bar}}} \quad \ldots *$$

And: $G = \mu_1 n_1 + \mu_2 n_2 \quad \ldots **$

$$G = \bar{G}_1 n_1 + \bar{G}_2 n_2$$

Hint. You can substitute $\bar{G}_1$ in ** to *

Recall: $\bar{G} = \overset{\Uparrow}{G_1^\circ} + RT\ln\frac{P_1}{1\,bar} = \mu_1^\circ + RT\ln\frac{P_1}{1\,bar}$

Note: $G = \bar{G}n_1 + \bar{G}_2 n_2$

$$G_{inital} = n_1\left(\mu_1^\circ + RT\ln\frac{P_1}{1\,bar}\right) + n_2\left(\mu_2^\circ + RT\ln\frac{P_2}{1\,bar}\right)$$

Note: $P_1 + P_2 = P$ only If there is no change In Volume as a result of mixing, that is: $\Delta_{mix}V = 0$. This condition holds for Ideal solns

$$G_{initial} = n_1(\mu_1^\circ + RT\ln P) + n_2(\mu_2^\circ + RT\ln P)$$

$$G_{final} = n_1(\mu_1^\circ + RT\ln P_1) + n_2(\mu_2^\circ + RT\ln P_2)$$

$$\Delta_{mix}G = G_{final} - G_{initial}$$

$$= n_1RT\ln\frac{P_1}{P} + n_2RT\ln\frac{P_2}{P}$$

$$= n_1RT\ln x_1 + n_2RT\ln x_2 \quad \text{.....} \ ****$$

Where; $P_1 = x_1P$ and $P_2 = x_2P$

$x_1$ & $x_2$ are the mole fractions of 1 and 2 respectively. [The standard chemical potential $\mu^\circ$ Is the same In the pure state and In the mixture).

$$x_1 = \frac{n_1}{n_1+n_2} = \frac{n_1}{n} \quad \boxed{\text{If } n_1 + n_2 = n}$$

$$x_2 = \frac{n_2}{n_1+n_2} = \frac{n_2}{n}$$

$n_1 = \underline{x_1 n}$ , $n_2 = x_2 n$.

Subtituting into equation ~~✱~~✱✱✱

$$n_1 RT \ln x_1 + n_2 RT \ln x_2.$$

$$\underline{n x_1} RT \ln x_1 + n x_2 RT \ln x_2.$$

$$nRT[x_1 \ln x_1 + x_2 \ln x_2].$$

$$\boxed{\Delta_{mix} G = nRT(x_1 \ln x_1 + x_2 \ln x_2)} \quad \text{...(i)}$$

Whee we have the change in Gibb's free energy with Temperature;

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \boxed{\Delta_{mix} S = -\frac{\Delta_{mix} G}{T}}$$

From ...(i)

$$\left(\frac{\partial \Delta_{mix} G}{\partial T}\right)_P = -\Delta_{mix} S = nR(x_1 \ln x_1 + x_2 \ln x_2)$$

$$\Delta_{mix} S = -nR(x_1 \ln x_1 + x_2 \ln x_2).$$ Entropy //

Now for Enthalpy;

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

$$\Delta_{mix} G = \Delta_{mix} H - T\Delta_{mix} S.$$

$$\Delta_{mix} H = \Delta_{mix} G + T\Delta_{mix} S.$$

$$= 0$$ Why? Because molecules of ideal gases do not interact with one another so no heat is absorbed / produced as a result of mixing

✓ ~~Example~~ Example 1: Calculate the Gibbs energy and entropy of mixing 1.6 moles of Argon at 1 atm and 25°C with 2.6 moles of nitrogen at 1 atm and 25°C. Assume Ideal behaviour.

## Solution.

Using: $\Delta_{mix} G = nRT(x_1 \ln x_1 + x_2 \ln x_2)$.

$Ar = 1.6$ moles  Nitrogen $= 2.6$ moles.

$$x_{Ar} = \frac{n_{Ar}}{n_A + n_{N_2}} = \frac{1.6}{1.6 + 2.6} = 0.38$$ [has no unit].

$$x_{N_2} = \frac{2.6}{1.6 + 2.6} = 0.62$$

~~$T = 273°C$~~ $T = 273 + 25 = 298K$.

$R = 8.314\ Jmol^{-1}K^{-1}$; $n = n_1 + n_2 = 4.2$ moles

$$\Delta_{mix} G = (4.2\text{ moles}) \times 8.314\ Jmol^{-1}K^{-1} \times 298K(0.38 \ln 0.38 + 0.62 \times \ln 0.62)$$

$\Delta_{mix} G = -6.9 kJ$.

Mistake: (Take note of "−")

$$\Delta_{mix} S = -\frac{\Delta_{mix} G}{T} = -\left(\frac{-6.9kJ}{298K}\right) = +23.15 J/k$$

$\Delta G = -ve$ = Spontaneous.

For reaction to proceed; there must be $\Delta S = +ve$

$\Delta G$ -ve

# Binary Mixture Of Volatile Liquid

The chemical potential for the liquid must be the same for a gaseous state.

$$\mu^*_{(l)} = \mu^*_{(g)}$$

i = for a Particular Specie

$$\mu_i = \mu_i^0 + RT\ln\frac{P}{1\,\text{bar}}$$

$$\mu^0_{(l)} = \mu^0_{(g)} = \mu^0_i + RT\ln\frac{P^*}{1\,\text{bar}}$$

[$P^*$ = Standard press

($\mu^0$ = Standard chemical potential at 1 bar)

For a two Component System (Liquid & gas)

$$\mu^0_{(l)} = \mu^0_{(g)} = \mu_1^0 + RT\ln\frac{P_1}{1\,\text{bar}}$$

$$\mu^0_{(l)} = \mu^0_{(g)} = \mu_2^0 + RT\ln\frac{P_2}{1\,\text{bar}}$$

$$\mu_{(l)} = \mu^0_{(l)} + RT\ln\frac{P_1}{P^*}$$

5th May 2025

$$\mu^*_{(l)} = \mu^*_{g} = \mu^\circ_{(g)} + RT\ln\frac{p^*}{1\,bar}$$

$$\boxed{\mu^*_{(l)} = \mu^*_{(g)}}$$

$$\mu_{(l)} = \mu_{(g)} = \mu^\circ_{(g)} + RT\ln\frac{P_1}{1\,bar}$$

$$\mu^*_{(l)} = \mu^*_{(g)} + RT\ln\frac{p^*}{1\,bar}$$

$$\mu_{(g)} = \mu^*_{(l)} - RT\ln\frac{p^*}{1\,bar} \quad \text{......(iii)}$$

$$\mu_{(l)} = \mu^*_{(l)} - RT\ln\frac{p^*}{1\,bar} + RT\ln\frac{P_1}{1\,bar}$$

$$\mu_{(l)} = \mu^*_{(l)} - RT\left(\ln\frac{p^*}{1\,bar} - \ln\frac{P_1}{1\,bar}\right)$$

$$= \mu^*_{(l)} + RT\left(\ln\frac{P_1}{1\,bar} - \ln\frac{p^*}{1\,bar}\right)$$

$$\mu_{(l)} = \mu^*_{(l)} + RT\ln\frac{P_1}{p^*} \quad \text{....(iv)}$$

## Raoult Law

$$\frac{P_1}{p^*} = x_1$$

$$\boxed{P_1 = x_1 p^*} \text{ — Raoult law}$$

The partial vapour pressure of a component of a solution is equal to the product of the mole fraction of the component and pressure of the free solution.

equation (V) into (iv)

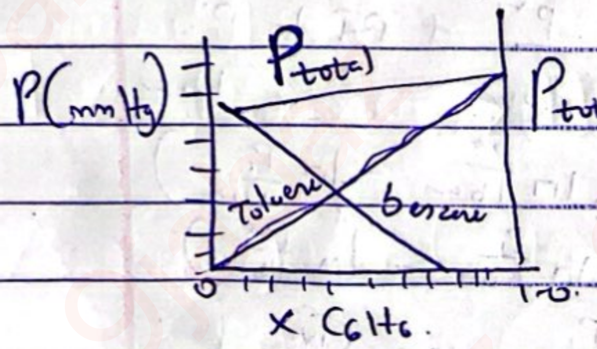
$\mu_{(l)} = \mu^*_{(l)} + RT \ln x_1$

In pure liquid,

$x_1 = 1$ then $\ln x_1 = 0$

$\therefore \mu_{(l)} = \mu^*_{(l)}$ only for an ideal solution.

Solution that OBEY RAOULT law are called ideal Solution e.g benzene & Toluene.



$P_{total} = P_{C_6H_6} + P_{C_7H_8}$

Question

liquid A & B form an ideal solution at 45°C, the Vapour pressure of pure A & B are 66 torr & 88 torr respectively. Calculate the composition of the Vapour In equilibrium with a solution Containing 36% mole at the temperature.

Solution

liq A $\longrightarrow$ 66 torr, $P_A^*$

liq B $\longrightarrow$ 88 torr; $P_B^*$

Solution = 36 mole percent A

$$\frac{36}{100} = 0.36$$

$X_A \Rightarrow$ mole fraction of A in the solution = 0.36

$X_B \Rightarrow$ mole fraction of B in the Solution = $1 - X_A$

$X_B = 1 - 0.36 = 0.64$

$P_A = 66$ torr, $P_B = 88$ torr, $X_A = 0.36$, $X_B = 0.64$

Partial pressure of A $(P_A^*) = X_A P_A^*$, ~~$P_B = X$~~

$P_B^* = X_B P_B^*$

$P_A^* = X_A P_A^*$

$P_A^* = 0.36 \times 66 = 23.6$ torr.

$P_B^* = 0.64 \times 88 = 56.3$ torr.

$P_T = P_A + P_B = 23.6 + 56.3 = P_T = 79.9$ torr.

$$x_A^v = \frac{P_A}{P_A + P_B} = \frac{P_A}{P_T} = \frac{23.6}{(23.6 + 56.3)\text{ torr}} = 0.3$$

$x_A^v = 0.3$

$$x_B^v = \frac{56.3}{(23.6 + 56.3)\text{ torr}} = 0.70 \qquad x_B^v = 0.70$$

An ideal solution made from 5 moles of benzene and 3.25 mole of toluene. Calculate $\Delta G$ of mixing and $\Delta S$ of mixing at 298 K and 1 bar pressure. Is the mixing a spontaneous process

$$x_{benzene} = \frac{5}{5+3.25} = 0.606$$

$$x_{toluene} = \frac{3.25}{5+3.25} = 0.394$$

$$n = 5 + 3.25 = 8.25$$

$$\Delta_{mix} G = nRT(x_{benzene} \ln x_{benzene} + x_{toluene} \ln x_{toluene})$$

$$\Delta_{mix} G = 8.25 \times 8.314 \times 298 (0.606 \ln 0.606 + 0.394 \ln 0.394)$$

$$= -13.623 \text{ KJ}$$

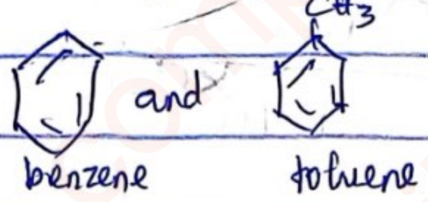
$$\Delta_{mix} S = -\frac{\Delta_{mix} G}{T} = -\left(\frac{-13624}{298}\right)$$

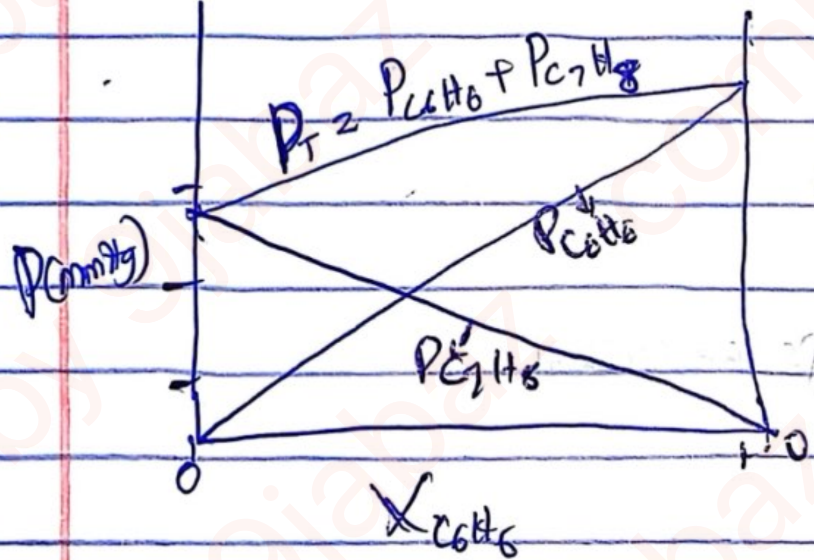
$$\Delta_{mix} S = 45.72 \text{ J/K}$$

Yes, the mixing is a spontaneous process. ($\Delta G < 0$, $\Delta S > 0$)

## Deviations from Raoult's Law

① Ideal situation

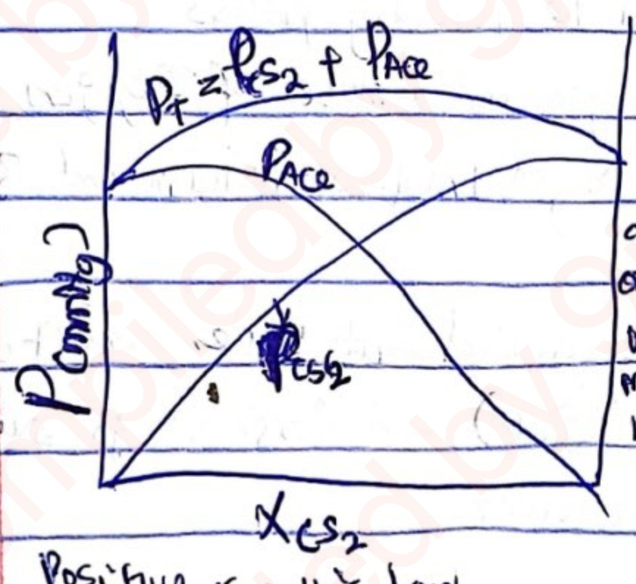




exact raoult law

+ve

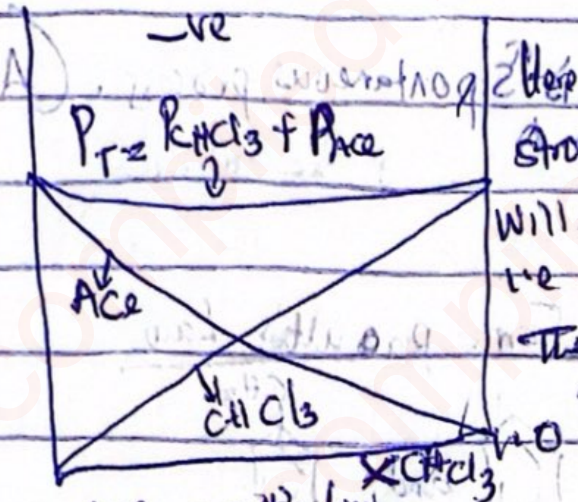
②



Force of attraction is weaker than the one of (benzene + toluene). Therefore, the addition of $CS_2$ and $ACe_2$ will be more than the normal additive number (e.g say 20ml of $CS_2$ and 20mL of Ace, the total which is supposed to be 40ml will be more than 40mL, i.e there will be increase in number of ml

Positive raoult's law

(iii)



negative raoult's law

Here, the force of attraction is stronger, due to this, there ~~negative raoult's law~~ will be decrease in the volume, i.e the volume shrinks. Therefore total P will be less than the addition of both

Henry's law

$P_2 = K x_2$

K = Henry's law constant

$P_2 = KM$

Examples

Calculate the ΔS for the following process

(a) mixing of 1 mole of Nitrogen and 1 mole of Oxygen

(b) Mixing of 2 moles of Argon, 1 mole of Helium and 3 moles of hydrogen.

Both a and b are carried out under condition of constant temperature (298K) and constant pressure

Assume ideal behaviour

## Note In note

Calculate the change in entropy for the following processes:

ⓐ Mixing of 1 mole of $N_2$ & 1 mole of $O_2$.

ⓑ Mixing of two moles of Ar, 1 mole of He, & three moles of H.

Both A & B are carried out under conditions of constant temperature 298K & constant pressure assume ideal behaviour.

Question 4)

Henry's law

1. Calculate the molar solubility of Carbon dioxide in $\overset{H_2O}{\text{water}}$ at 298K and $CO_2$ pressure of $3.30 \times 10^{-4}$ atm which corresponds to the partial pressure of $CO_2$ in air. The [Henry's law constant (K) for $CO_2 = 1.24 \times 10^{6}$ torr].

$[K' = 29.3 \text{ atm mol}^{-1}\text{ kg}]$

# Henry's law

Solution ⇒ Solute + Solvent.

1 2.

$P_2 = Kx_2$. ; K = Henry's law constant.

P

$P_2 = K'm$ $P_1 = x_1 P_1^*$ m = molality.

## Solution to question ①

$P_{CO_2} = Kx_{CO_2}$ ⇒ Henry's law

$$x_{CO_2} = \frac{P_{CO_2}}{K}$$

$\boxed{n_{CO_2} \ll n_{H_2O}}$

$$x_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{H_2O}} = \frac{n_{CO_2}}{n_{H_2O}}$$

$$\frac{n_{CO_2}}{n_{H_2O}} = \frac{P_{CO_2}}{K}$$

$$n_{CO_2} = \frac{n_{H_2O} P_{CO_2}}{K} \Rightarrow 1\,atm = 760\,torr$$

$$n_{CO_2} = (760\,torr \times 3.3 \times 10^{-4}) \times \frac{1000g}{18g\,mol^{-1}} \times \frac{1}{1.24 \times 10^6\,torr}$$

$$= 1.12 \times 10^{-5}\,mol$$

$$n_{H_2O} = \frac{m_{H_2O}}{Mm_{H_2O}}$$

$$m = 1.12 \times 10^{-5}\,mol\,(kg\,H_2O)^{-1}$$

$$= \frac{1000g}{18g/mol}$$

OR

$P_2 = k'm$

$$m = \frac{P_2}{k'} = \frac{3.3\times10^{-6}\ \text{atm}}{29.3\ \text{atm mol}^{-1}\ \text{Kg}} =$$

*

② The average human with a 70kg has ~~Pass~~ a blood volume of 5.00L. The Henry's law constant for the Solubility of $N_2$ in water is $9.04\times10^{4}$ bar at 298K. Assume that this is also the value of the Henry's Law constant for blood and that the density of blood = 1.0kg/L. Calculate the no of moles of nitrogen absorbed In this amount of blood in air of composition of 80% $N_2$ at sea-level where the pressure is 1 bar and at pressure of 50 bar.

Solution.

$$x_{N_2} = \frac{P_{N_2}}{K}$$

Where - The partial pressure

$$x_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{H_2O}}$$

total pressure = 1 bar.

$N_2$ is 80% of air

$$P_T\ (1\ \text{bar}) = \boxed{P_{N_2}} + P_{other}$$ ✓

$$\text{Density} = \frac{\text{mass}}{\text{Volume}}$$

$$m = DV = 1\,\text{kg}\,\cancel{L}^{-1} \times 5.00\,\cancel{L} = 5\,\text{kg}.$$

$K = 9.04 \times 10^4 \text{bar}$

Volume = 5.00L.

$\rho = 1.0\text{kg/L}$ ~~of~~ blood = $\rho$ of $H_2O$.

Mass of $H_2O$ = mass of water why?

$\text{mass}_{bld} = \rho_{bld} \times V_{bld} = 5.0 \times 10^3 g$ (bld = blood)

$P_{N_2} = K x_{N_2}$

$x_{N_2} = \frac{P_{N_2}}{K}$

$x_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_w} = \frac{n_{N_2}}{n_w}$

$n_w \gg n_{N_2}$

$\frac{n_{N_2}}{n_w} = \frac{P_{N_2} n_w}{K}$

Note: 80% of 1bar
80% of 50 bar

$n_w = \frac{5000g}{18.02 g mol^{-1}} = \frac{mass}{molar\ mass}$

$m = 5000g.$

$n_{N_2} = \frac{5 \times 10^3 g}{18.02 g mol^{-1}} \times \frac{0.8 bar}{} = 2.5 \times 10^{-3} mol$

Pressure at 50bar = $2.5 \times 10^{-3}$ mol $\times 50$

## Real Solutions

Note: Ideal Solution DOES NOT EXIST.

Recap: Ideal solution $\mu(l) = \mu^*(l) + RT\ln x_1$ ✓

Real solution $\mu(l) = \mu^*(l) + RT\ln a$.

Ideal situation: Solvent ⇒ Raoult's law

Solute ⇒ Henry's law

$$x_1 = \frac{P_1}{P_1^*}$$

$P_1$: Partial pressure of one solution

$P_2$: Partial pressure of free solvent

For any liquid, if $x_1 \rightarrow 1$, $\underset{\uparrow \text{ activity.}}{a_1} \rightarrow 1$.

$$a_1 = \frac{P_1}{P_1^*}$$

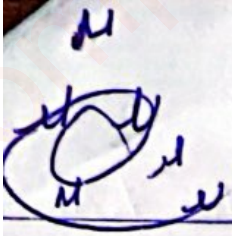
$a_1 = \gamma_1 x_1 \Rightarrow$ $\gamma_1$ = activity coefficient

$x_1$ = solvent composition

For Real solution:

$$\mu(l) = \mu^*(l) + RT\ln a_1$$

$$\mu(l) = \mu^*(l) + RT\ln \gamma_1 x_1$$



$$\boxed{\mu_{(l)} = \mu^*_{(l)} + RT\ln\gamma_1 + RT\ln x_1}$$

## For Solute

$$a_2 = \frac{P_2}{P_2^*}$$

$$\mu_{(l)} = \mu^*_{(l)} + RT\ln\left(\frac{P_2}{P_2^*}\right)$$

$$\mu_{(l)} = \mu^*_{(l)} + RT\ln\left(\frac{Kx_2}{P_2^*}\right)$$

$$\mu_{(l)} = \mu^*_{(l)} + RT\ln\frac{K}{P_2^*} + RT\ln x_2$$

$$= \mu^*_{(l)} + RT\ln\frac{K}{P_2^*} = \mu^\circ_{(l)}$$

$$P_2 = Kx_2.$$

$$\mu_{(l)} = \mu^\circ + RT\ln x_2.$$

## Question

Calculate an activity coefficient for Carbon disulphide at $x_{CS_2} = 0.3502$ Given that:

; $P_{CS_2} = 358.3$ torr ⇒ Partial pressure of $CS_2$

(i) $P^*_{CS_2} = 512.3$ torr ⇒ Vapour pressure of Carbon disulphide is 512.3 torr

**Solution**

$$a_{CS_2} = \frac{P_{CS_2}}{P^*_{CS_2}} = \frac{358.3 \text{ torr}}{512.3 \text{ torr}} = 0.6994.$$

$$\gamma_{CS_2} = \frac{a_{CS_2}}{x} = \frac{0.6994}{0.3502} = 1.997.$$

**Quiz**

* With the aid of Sketches, and with specific examples, briefly explain positive ~~dead~~ and negative deviation for Raoult's law

Quests.

① The vapour pressure of n-propanol ~~at 298K~~ and water at 298K are 21.8 and 23.8 mmHg respectively. In a solution In which the mole fraction of water is 0.20, their partial pressure are 17.8 and 13.4 mmHg respectively, Calculate the activity (a) and activity Coefficients ($\gamma_i$) of the two components In each solution.

② The mole fraction of a non-Volatile solute In water is 0.01 If the equilibrium vapour pressure of pure water at 293K is 2.334 kPa and that of the solution is 2.269 KPa, Calculate the activity and activity coefficient of water.

ⓑ Is the water in this solution acting ideally or close? Give a reason for your answer..

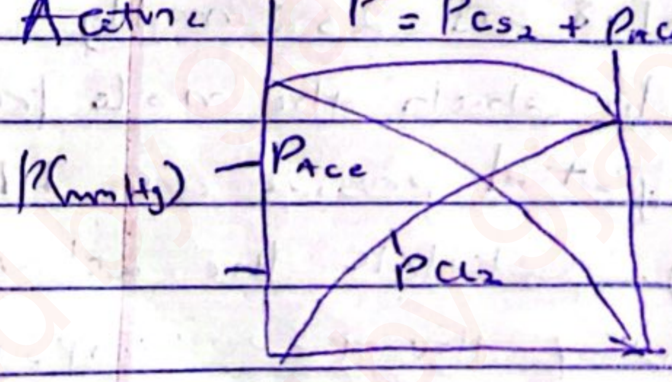
## Deviations from Raoult's law

In an Ideal solution, because molecules are alike then there is no Intermolecular attraction, Then the molecules are additive.

Example:

50ml of $H_2O$ + 50mL (Ethanol).

For positive deviation: We have below: e.g Carbondisulphide and Acetone



This is for Acetone and $CS_2$

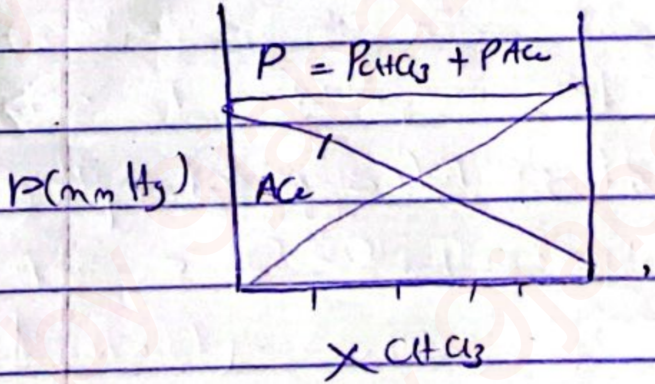
The ~~force of~~ attraction

Most Solutions do not behave ideally. The positive deviation corresponds to the case in which the Intermolecular forces between unlike molecules are weaker than those between like molecules and there is a greater tendency for these molecules to leave the solution than in the case of an Ideal solution. Consequently, the Vapour pressure of the solution is greater than the sum of the vapour pressure for an Ideal Solution

**Negative Deviation**

~~Example~~: Chloroform — Acetone [$CHCl_3 - CH_3COCH_3$]

Just the opposite of positive deviation, holds for a negative deviation from Raoult's law. In this case, unlike molecules attract each other more strongly than they do their own kind, and the Vapour pressure of the solution is less than the sum of the Vapour pressure from an Ideal solution



Note: Since there is a stronger force of attraction, there will be a shrink in volume then a decrease in pressure.

Example: class :

Calculate the change in entropy of the following processes:

ⓐ Mixing of 1 mole of $N_2$ and 1 mole of $O_2$

ⓑ Mixing of 2 moles of Argon, 1 mole of Helium & 3 moles of Hydrogen.

Both A & B are carried out under conditions of Constant temperature i.e 298K & Constant pressure. Assume Ideal behaviour.

**Note**:- Henry's law is only applicable to dilute solutions. They can mix and form chemical bond. (but each of the components cannot be gotten as solute from the solution).

**Example 4**: Calculate the molar solubility of Carbon dioxide in water at 298K and $CO_2$ pressure of $3.3 \times 10^{-4}$ atm, which corresponds to the partial pressure of $CO_2$ in air. The Henry's law constant, K for $CO_2$ is given as $1.24 \times 10^{6}$ torr ($K'$ is 29.3 atm $mol^{-1}$ kg of water)

Solution

The mole fraction of solute $CO_2$ is given as:

$$X_{CO_2} = \frac{P_{CO_2}}{K}$$

Because the no of moles of $CO_2$ dissolved in 1000g of water is small, we can approximate the mole fraction as follow:

$$X_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{H_2O}} = \frac{n_{CO_2}}{n_{H_2O}}$$

$$n_{CO_2} = \frac{P_{CO_2} n_{H_2O}}{K}$$ ✓

finally,

$$n_{CO_2} = (3.3 \times 10^{-4} \times 760)\,\text{torr} \times \frac{1000g}{18.01\,g\,mol^{-1}} \times \frac{1}{1.24 \times 10^{6}\,\text{torr}}$$

$$= 1.12 \times 10^{-5}\,mol.$$

Note: 1 atm = 760 torr

Because this is the no of moles of $CO_2$ in 1000g or 1kg of $H_2O$ the molality is:

$$1.12 \times 10^{-5}\,mol\,(kg\,H_2O)^{-1}$$

Alternatively

We can use equation (24) and proceed as follows:

$$m = \frac{P_{CO_2}}{K'} = \frac{3.3 \times 10^{-4}\,atm}{29.3\,atm\,mol^{-1}\,kg\,H_2O} = 1.12 \times 10^{-5}\,mol\,kg\,(H_2O)^{-1}$$

Example 5: Done ✓

~~12-05-2025~~

## Colligative Properties

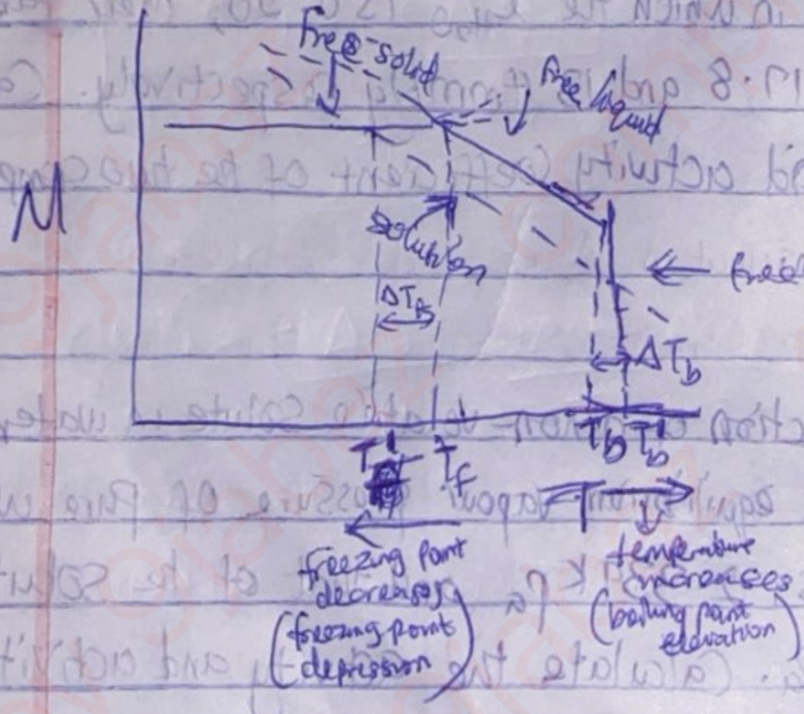
i. Boiling - point elevation

ii. Freezing - point depression

iii. Osmotic pressure

$\mu_{(l)} = \mu^*_{(l)} + RT \ln x_1 \Rightarrow \mu_{(l)} - \mu^*_{(l)} = RT \ln x_1$

$\Rightarrow \Delta \mu_{(l)} = RT \ln x_1$



$x_1 = \frac{P_1}{P_1^*} \Rightarrow x_1 + x_2 = 1$

$x_1 = 1 - x_2$

$x_1 = 1 - x_2 = \frac{P_1}{P_1^*}$

$P_1 = P_1^*(1 - x_2)$

$P_1 = P_1^* - x_2 P_1^* \Rightarrow P_1 - P_1^* = -x_2 P_1^*$

~~$P_1^{sln} = P_1 - x_2 P_1^*$~~

$$\boxed{\Delta P_1 = x_2 P_1^*}$$

~~$\Delta T_b = K_b m$~~

$\Delta T_f = $ [illegible] $p\,d$

$\mu_{1(l)} = \mu^*_{1(l)} + RT\ln x_1$

$\mu_{1(l)} = \mu_{1(g)} = \mu^*_{(l)} + RT\ln x_1$

$\mu_{1(g)} - \mu^*_{(l)} = RT\ln x_1$

$\Delta\mu_1 = RT\ln x_1$

$\Delta\mu_1 = \Delta_{vap}\bar{G}$

~~$\Rightarrow \Delta_{vap}\bar{G} = RT\ln x_1 T$~~

$\Rightarrow \Delta_{vap}\bar{G} = \mu_{1(g)} - \mu^*_{(l)} = RT\ln x_1$

Dividing by $T$

$$\frac{\Delta_{vap}\bar{G}}{T} = \frac{\mu_{1(g)} - \mu^*_{(l)}}{T} = R\ln x_1$$

Gibbs - Helmholtz Equation

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

$$\frac{d(\Delta G/T)}{dT} = \frac{-\Delta H}{T^2} \quad (\text{at constant } p)$$

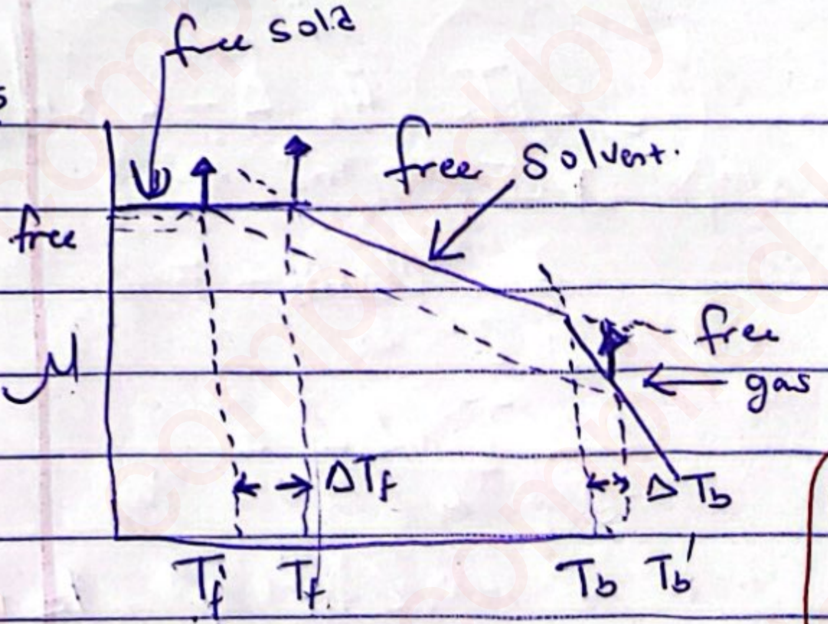
$$\frac{d(\Delta_{vap}\bar{G}/T)}{dT} = \frac{-\Delta_{vap}\bar{H}}{T^2} = R\frac{d(\ln x_1)}{dT}$$

$$\int_{\ln 1}^{\ln x_1} d\ln x_1 = \int_{T_b}^{T'_b} -\frac{\Delta_{vap}\bar{H}}{RT^2}\, dT$$

$$\ln x_1 = -\frac{\Delta_{vap}\bar{H}}{R}\,\frac{\Delta T}{T_b^2}$$

where
$\Delta T = T'_b - T_b$

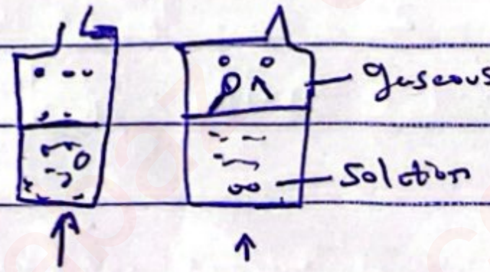
13/05/2025



ΔTf = freezing point depression !.

Note: Initial = $T_f'$
final = $T_f$

Initial = $T_b$
final = $T_b'$

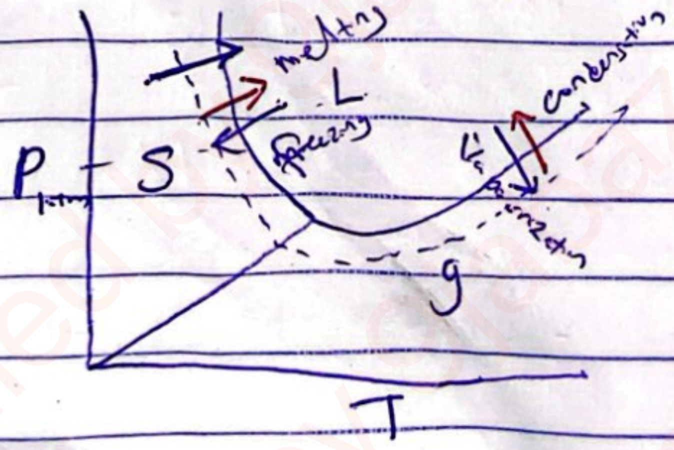


In a Solution, At boiling point you see equilibrium

$\Delta T_b$ = Boiling point depression

for example: Show that: $\Delta T_b = Km_2$
: $\Delta T_f = Km_2$

Note: $\Delta \mu_1 = \Delta \bar{G}$ from: $\mu_i = \bar{G}_i$



S-G
~~Condens~~
Sublimation

Solid - liquid = melting
Liquid - gas ⇒ Vaporation

$$\Delta\mu = \Delta_{vap}\bar{G}$$

$$\Delta\bar{G} = \mu_{(g)} - \mu^*(l) = RT\ln x_1$$

$$\frac{\Delta G}{T} = \frac{\mu_1(g) - \mu^*(l)}{T} = R\ln x_1$$

Gibb's Helmoltz equatn.

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_p = \frac{-\Delta H}{T^2} \text{ ; At constant P}$$

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_P = \frac{R\partial\ln x_1}{\partial T} = R\frac{\partial \ln x_1}{\partial T}$$

$$d\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{dT}\right] = -\frac{\Delta\bar{H}}{T^2}$$

$$-\frac{\Delta_{vap}\bar{H}}{T^2} = R\frac{\ln x_1}{dT}$$

$$d\ln x_1 = -\frac{\Delta_{vap}\bar{H}\,dT}{RT^2}$$

$$\int_{\ln 1}^{\ln x_1} d\ln x_1 = -\int_{T_b}^{T_b'} \frac{\Delta_{vap}\bar{H}\,dT}{RT^2}$$

$$\ln x_1 = \frac{\Delta_{vap}\bar{H}}{R}\left(\frac{1}{T_b'} - \frac{1}{T_b}\right)$$

$$\ln x_1 = -\frac{\Delta_{vap}\bar{H}}{R}\left(\frac{T_b' - T_b}{T_b' T_b}\right)$$

$$= -\frac{\Delta_{vap}\bar{H}}{R}\frac{\Delta T}{T_b' T_b}$$

$$= -\frac{\Delta_{vap}\bar{H}}{R}\frac{\Delta T}{T_b^2}$$

$x_1 = 1 \Rightarrow$ In a free state

$x_1 + x_2 = 1$ ; $x_1 = (1 - x_2)$

$$\ln x_1 = \ln(1 - x_2) = -\frac{\Delta_{vap}\bar{H}}{R}\frac{\Delta T}{T_b^2}$$

Maclaurin's Series:

$$\ln(1 - x_2) = -x_2 - \frac{x_2^2}{2} - \frac{x_2^3}{3} \Rightarrow = -x_2.$$

$$(x_2 << 1)$$

$$\ln(1 - x_2) = -x_2 = -\frac{\Delta_{vap}\bar{H}}{R}\frac{\Delta T}{T_b^2}$$

$$x_2 = \frac{\Delta_{vap}\bar{H}}{R}\frac{\Delta T}{T_b^3}$$

$$\Delta T = \frac{R T_b^2 x_2}{\Delta_{vap}\bar{H}}$$

$$x_2 = \frac{n_2}{n_1 + n_2} \simeq \frac{n_2}{n_1}$$

$$x_2 = \frac{n_2}{n_1} = \frac{n_2}{w_1/M_1}$$ Hint $\left[ w_1/M_1 = \frac{\text{mass}}{\text{molar mass}} \right]$

$$\frac{n_2}{n_1} = \frac{n_2 M_1}{w_1} = \frac{n_2}{w_1} M_1$$

Note: Molality = no of mole of solute / ~~mass of~~ solvent . In 1kg,

$$\therefore \frac{n_2}{w_1} = \text{Molality.} = m_2 \quad \left[ \text{where } m_2 = \text{molality} \right]$$

$$x_2 = \frac{n_2}{n_1} = m_2 M_1$$

$$x_2 = \boxed{\frac{n_2}{n_1} = m_2 M_1}$$

$$\Delta T = \frac{RT_b^2}{\Delta_{vap}\bar{H}} m_2 M_1$$

$$\therefore \Delta T = \frac{RT_b^2}{\Delta_{vap}\bar{H}} M_1 m_2 .$$

$$\Rightarrow \cancel{\frac{RT_b^2}{\Delta H_{x M_1}}} \Rightarrow \frac{RT_b^2}{\Delta_{vap}\bar{H}} M_1 = K$$

$$\therefore \Delta T = K m_2$$

$$\Delta T = K_b m_2 .$$

You Can be asked!!

For freezing Point depression

$$\Delta T = \frac{RT_f^2 M_1 m_2}{\Delta_{freez}\bar{H}} = K_f m_2$$

14/05/2025

Note $\boxed{x_1 < 1}$

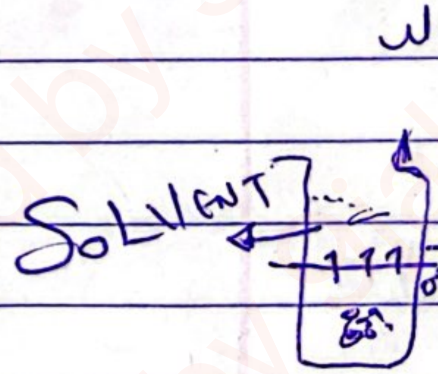
$$\mu_1 = \mu^*(l) + RT\ln x_1$$

$$x_1 + x_2 + x_3 \ldots + x_n = 1$$

$$\frac{n_1}{\Sigma n} + \frac{n_2}{\Sigma n} \ldots + \frac{n_z}{\Sigma z} = 1.$$ [For A solution]

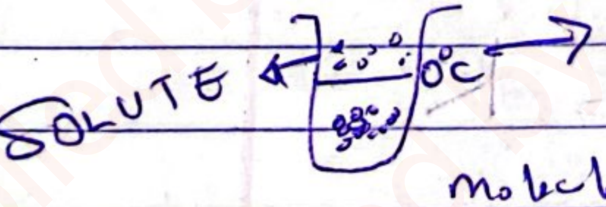
For Only one Component;

$$\mu(l) = \mu^*(l) + RT\ln(1)$$

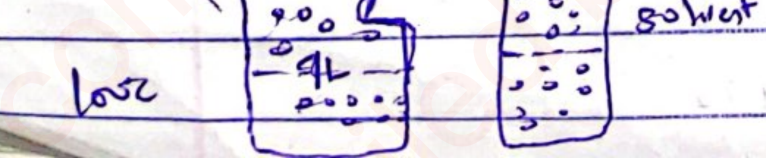


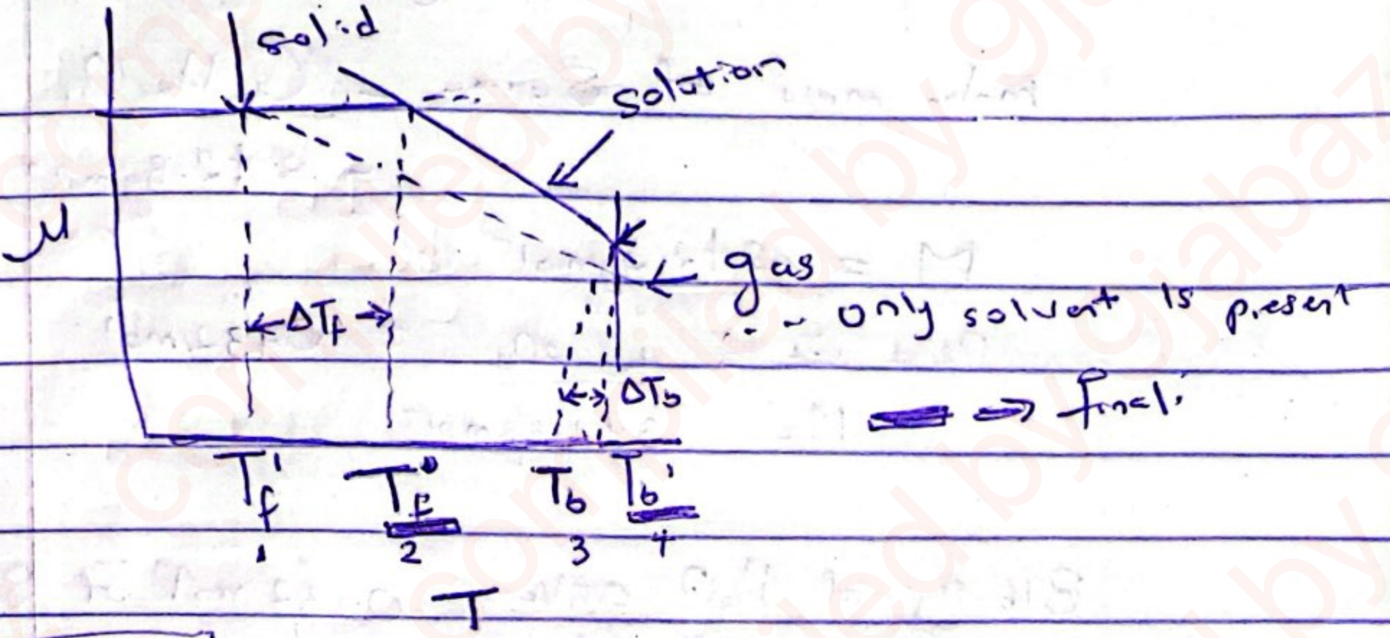
→ Only solvent molecules are present at the exact boiling point.

→ Interface → A kind of equilibrium



→ When solute is present at the boiling point, because there is a molecule of the solid and it also close to the Interface, it will not allow freezing at that particular temperature.





$\boxed{\Delta T_f = -1}$ $\Delta T_f$ = freezing point depression

$T_f' - T_f = 1 - 2 = -1 \Rightarrow$ Decrease

$\Delta T_b = T_b' - T_b$

eg: $4 - 3 = 1$.

Question

For a solution of 45.20g of sucrose in 316.0g of water. Calculate:

ⓐ The boiling point

ⓑ The freezing point

$(K_b \ \& \ K_f)_{water} = 0.51 \text{ K mol}^{-1}\text{kg} \ \& \ 1.86 \text{ K mol}^{-1}\text{kg}$ respectively.

Solution

$\Delta T = K_b m_2$

$w_1$ = mass of $H_2O$ = 316.0g

$w_2$ = mass of Sucrose = 45.20g.

$K_b = 0.51 \text{ K mol}^{-1}\text{kg}$

$K_f = 1.86 K mol^{-1} kg$.

molar mass of Sucrose = $C_{12}H_{22}O_{11}$

$= 342.3 g mol^{-1}$

$M = 342.3 g mol^{-1}$

$$n_2 = \frac{w_2}{M_2} = \frac{45.20 g}{342.3 g mol^{-1}} = 0.132 mol$$

316.0g of $H_2O$ contains 0.132 mol of Sucrose

1000g of $H_2O$ $\longrightarrow$ $x$

$$\cancel{x = \frac{1000 g \times 0.132 mol}{316.0 g}}$$

$$x = \frac{1000 g/Kg \times 0.132 mol}{316.0 g}$$

$x = 0.4178 mol/Kg$ of $H_2O$

$\therefore m_2 = 0.418 mol/kg$ of $H_2O$.

$\Delta T = 0.51 K mol^{-1} kg \times 0.418 mol kg^{-1}$

$\Delta T = 0.213 K$

Note: water boils at 100°C = 373K

$0°C = 273.15 K$

$\Delta T = T_b' - T_b$

$T_b' = \Delta T + T_b = 373.15 K + 0.213 K$

$T_b' = 373.363 K.$

$\Delta T = K_f m_2$

$\Delta T = T_f' - T_f.$

$T_f' = T_f + \Delta T \Rightarrow$

$\Delta T = 1.86 K \cancel{mol^{-1} kg} \times 0.418 \cancel{mol} \cancel{kg^{-1}}$

$\Delta T = 0.777 K.$

$T_f' = \Delta T + T_f.$

$= -273.15 K - 0.777 K$

$= -272.32 K$

19th May, 2025

## Osmotic Pressure

The dissolution of a 4.5g substance in 25g of $CCl_4$ leads to an elevation of 0.650K. calculate

(a) The freezing point depression

(b) The molar mass of the substance

(c) The factor by which the vapour pressure to which $CCl_4$ is lowered. ($K_f = 30\ Kmol^{-1}kg$, $K_b = 4.95\ Kmol^{-1}kg$

Solution

$w_2 = 4.5g$, $w_1 = 25g$ ($CCl_4$), $\Delta T_b = 0.650K$

$M_1 = 153.8\ g\,mol^{-1}$  $\Delta T_f = ?$

(a) $\Delta T_b = K_b m_2$

$$m_2 = \frac{\Delta T_b}{K_b}$$

$$\Delta T_f = K_f m_2$$

$$m_2 = \frac{\Delta T_f}{K_f}$$

$$m_2 = \frac{\Delta T_b}{K_b} = \frac{\Delta T_f}{K_f}$$

$$\Delta T_f = \frac{\Delta T_b K_f}{K_b}$$

$$\Delta T_f = \frac{-0.650K \times 30\ Kmol^{-1}kg}{4.95\ Kmol^{-1}kg}$$

$\Delta T_f = -3.94K$

(b) $m_2 = \frac{n_2}{1kg\ CCl_4}$

$m_2$ = molality, $w_2$ = mass of solute

$n_1$ = no of mole of solvent

$w_1$ = mass of solvent

$M_1$ = molar mass of $CCl_4$

$$m_2 = \frac{n_2}{w_1(kg)} = \frac{\frac{w_2}{M_2}}{w_1}$$

$$m_2 = \frac{w_2}{M_2 w_1} \Rightarrow \frac{\Delta T_b}{K_b} = \frac{w_2}{M_2 w_1}$$

$$\Rightarrow \Delta T_b = K_b\left(\frac{w_2}{M_2 w_1}\right)$$

$$M_2 = \frac{K_b w_2}{\Delta T_b w_1}$$

$$M_2 = \frac{4.95\,K\,mol^{-1}\,kg \times 4.50g}{0.125kg \times 0.650K}$$

$M_2 = 274\ g\,mol^{-1}$

ⓒ We are to calculate the mole fraction

$x_1 = \frac{P_1}{P_1^*}$   $x_1$ is higher in a free solvent than in solution.

$x_1 + x_2 = 1$

$x_1 = 1 - x_2$

$x_2 = \frac{n_2}{n_1 + n_2}$

$\cancel{x_1 = \frac{n_2}{n_1 + n_2}}$ $(1 - x_2) = \left(1 - \frac{n_2}{n_1 + n_2}\right)$

$\boxed{x_1 = 1 - x_2}$

$x_1 = 1 - \frac{n_2}{n_1 + n_2}$

$\cancel{x_1 = 1 - \frac{w_2}{M_2}}$   $x_1 = 1 - \frac{\frac{w_2}{M_2}}{\frac{w_1}{M_1} + \frac{w_2}{M_1}}$

$\Rightarrow x_1 = 1 - \frac{\frac{4.50g}{274\,gmol^{-1}}}{\left(\frac{125g}{183.8\,gmol^{-1}}\right) + \left(\frac{4.50g}{274\,gmol^{-1}}\right)}$

$x_1 = 0.980$

## CHM 304 MID-SEMESTER TEST (2023-2024 SESSION)

**Time allowed: 30 min.**

1. Which of the following has a higher chemical potential? If neither, answer "same". (a) $H_2O(s)$ or $H_2O(l)$ at water's normal melting point, (b) $H_2O(s)$ at – 5°C and 1 bar or $H_2O(l)$ at – 5°C and 1 bar, (c) benzene at 25°C and 1 bar or benzene in a 0.1 M toluene solution in benzene at 25°C and 1 bar.
2. At 45°C, the vapour pressure of water is 65.76 mmHg for a glucose solution in which the mole fraction of glucose is 0.080. calculate the activity and activity coefficient of the water in the solution. The vapour pressure of pure water at 45°C is 71.88 mmHg.
3. Calculate the molal boiling-point elevation constant ($K_b$) for water. The molar enthalpy of vaporization ($\Delta_{vap}\overline{H}$) of water is 40.79 kJ $mol^{-1}$ at 100°C. $R = 8.314$ J $mol^{-1}$ $K^{-1}$, molar mass of water is 18.02 g $mol^{-1}$.

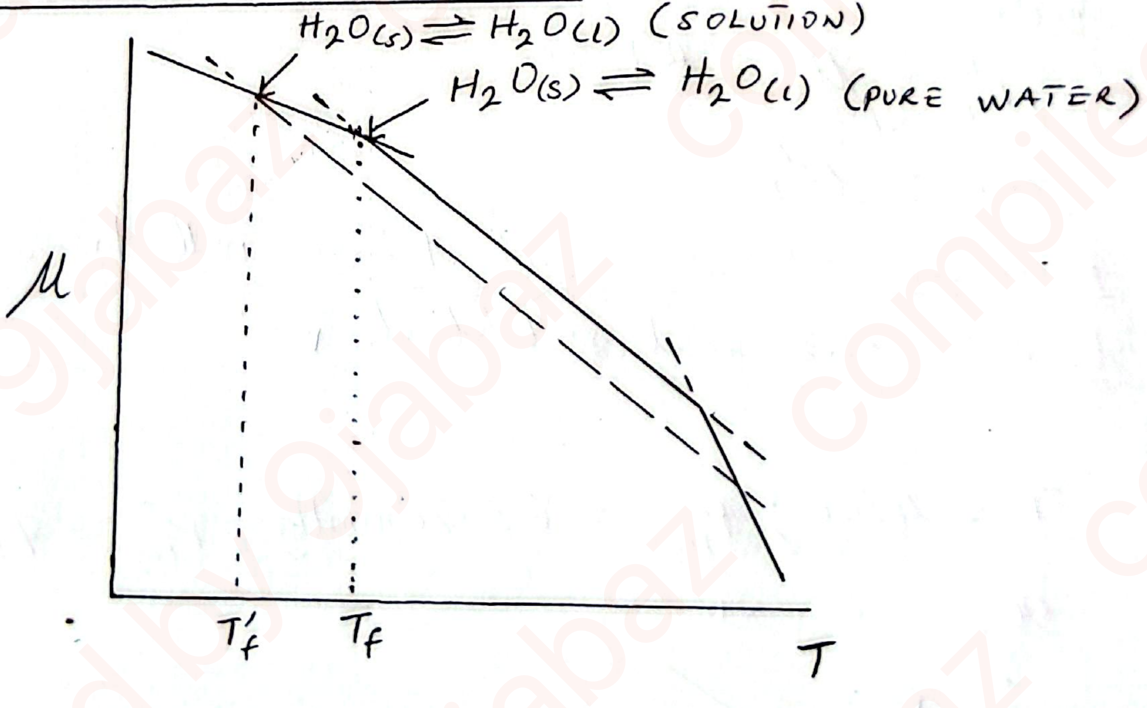
# CHM 304 SOLUTION TO TEST QUESTIONS

1(a) $H_2O(s)$ and $H_2O(l)$ at water's normal melting point.

— At normal melting point (0°C) both $H_2O(s)$ and $H_2O(l)$ are at equilibrium. Therefore, they have the same chemical potential. ✓

(b) $H_2O(s)$ and $H_2O(l)$ both at -5°C and 1 bar

— This is an indication that the $H_2O$ contains a nonvolatile solute (dissolved in it) that depresses it's freezing point to -5°C. In the solution, $H_2O(s)$ and $H_2O(l)$ are at equilibrium. Therefore, both will have the same chemical potential ✓



(c) Both benzene and benzene in solution with 0.1M toluene are at 25°C and 1 bar.

NB: The solution of benzene and toluene is nearly ideal, NOT ideal!

⇒ If $\mu_b$ represents the chemical potential of benzene in a single component solvent, and $\mu_b^L$ represents the chemical potential of benzene in solution with 0.1 M toluene, then,

$$\mu_b = \mu_b^* + RT \ln x_1$$

For a single component solvent, $x_1 = 1$.

$$\therefore \mu_b = \mu_b^*$$

In solution with 0.1 M toluene,

$$\mu_b^L = \mu_b^* + RT \ln x_1 \qquad (x_1 < 1)$$

$$\therefore \quad = \mu_b^* + RT \ln (1 - x_2)$$

$$= \mu_b^* - RT x_2 \qquad (\ln(1 - x_2) = - x_2$$

$$\therefore \text{If } \mu_b = \mu_b^*$$

Then,

$$\mu_b^L = \mu_b - RT x_2$$

$$\mu_b > \mu_b^L$$

$\therefore$ Benzene at 25°C and 1 bar will have a higher chemical potential ✓

2. $T = 45°C$; $P_{H_2O} = 65.76 \text{ mmHg}$; $P^*_{H_2O} = 71.88 \text{ mmHg}$

$$x_2 = 0.080.$$

$$a = \frac{P_{H_2O}}{P^*_{H_2O}} ✓ = \frac{65.76 \text{ mmHg}}{71.88 \text{ mmHg}} = 0.9149 ✓$$

$$a = \gamma x_2$$

$$\gamma = \frac{a}{x_1}. ✓$$

$x_1 + x_2 = 1$.

$x_1 = 1 - x_2$

$= 1 - 0.080 = 0.92$

$\gamma = \frac{a}{x_1} = \frac{0.9149}{0.9200} = 0.9945$ ✓

(3) $K_b = \frac{RT_b^{\,2} M_1}{\Delta_{vap}\bar{H}}$

$R = 8.314\,\text{J mol}^{-1}\text{K}^{-1}$; $T_b = (100 + 273)\,\text{K} = 373\,\text{K}$;

$M_1 = 18.02\,\text{g mol}^{-1} = 0.01802\,\text{kg mol}^{-1}$

substituting these values into the equation.

$K_b = \frac{(8.314\,\text{J mol}^{-1}\text{K}^{-1})(373\,\text{K})^2(0.01802\,\text{kg mol}^{-1})}{40{,}790\,\text{J mol}^{-1}}$ ✓

$K_b = 0.511\,\text{kg mol}^{-1}\,\text{K}$. ✓