Print Notes – Installment 1
Chem 123 Winter 2003 – Rossi

Colligative Properties (some of them)

- **Boiling Point Elevation**
- **Freezing Point Depression**
- **Osmotic Pressure**

  All of phenomena listed above depend on the concentration of solute particles in a solvent, but not their identity. The use of the terminology "number of particles" is important, because for things that break up to form more than one particle in solution the effective concentration is higher than the concentration of the formula unit used. For example, since NaCl (table salt) breaks up to form Na^+ and Cl^- ions in an aqueous solution, a 1 molal solution of NaCl in water will have about the same colligative effect as a 2 molal solution of something that does not break up in water, like sugar. An effect called "ion-pairing" can cause the number of free particles floating around a salt solution to be a little less than two per NaCl. A few of the NaCl are stuck together as a single particle at any given point in time.

Example: H_2 combustion in a Magic Syringe

Say we start with 1.00 mol of H_2 and 1.00 mol of O_2 in a magic syringe located in an ambient pressure of 26.0 atm and at a temperature of 280 K. A spark is used to ignite the H_2 and O_2, so that (complete) combustion occurs. How much work is done by the expanding gas? How much heat will have been released to the surroundings once the syringe's contents have cooled back to the ambient temperature? [Assume the pressure on the syringe piston remains constant at 26.0 atm during the explosion!] The standard heat of combustion for H_2, 286 kJ/mol, which is the absolute value of the standard enthalpy of formation for $H_2O_{(\ell)}$, $-286\ \text{kJ}\cdot\text{mol}^{-1}$.

Chemical reaction: $H_{2(g)} + O_{2(g)} \rightarrow H_2O_{(\ell)}$ Balanced: $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)}$ H_2 is the limiting reagent

Work = W = $P_{ext}\cdot\Delta V$ $P_{external}$ = Pressure on piston = 26.0 atm $\Delta V = V_{final} - V_{initial}$ (Get these from $PV=\eta RT$)

Assume: The H_2 and O_2 are ideal gases; the H_2O will be a liquid at 280 K (6.85·C) and will take up almost no volume.

Initially, there is a total of 2.00 mmol of ideal gas at 26.0 atm and 280 K. Using the ideal gas law, the initial volume must be

$$V_{initial} = \frac{\eta_{total}RT}{P} = \frac{(2.00\,\text{mol})(0.08206\,\ell\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(280\text{K})}{26.0\,\text{atm}} = 1.76_7\ \ell$$

When the gases are ignited, all the H_2 will be consumed, producing an equal number of moles of liquid H_2O:

$$1\ \text{mol}\ H_2\left(\frac{2\ \text{mol}\ H_2O}{2\ \text{mol}\ H_2}\right) = 1\ \text{mol}\,H_2O\left(\frac{18.02\ \text{g}\ H_2O}{1\ \text{mol}\ H_2O}\right)\left(\frac{1\ \text{m}\ell\,H_2O}{1\ \text{g}\ H_2O}\right) = 18.02\,\text{m}\ell\ =\ 0.01802\ \ell$$

There will be 0.50 moles of O_2 left over, and once they cool back down to 280 K, they will occupy a volume of

$$V_{O_2} = \frac{\eta_{O_2}RT}{P} = \frac{(0.50\,\text{mol})(0.08206\,\ell\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(280\text{K})}{26.0\,\text{atm}} = 0.44_2\ \ell$$

The final volume will be that occupied by the liquid water and the gaseous O_2 will be:

$$V_{final}\ =\ V_{water} + V_{extra\ oxygen}\ =\ 0.01802\ \ell + 0.44_2\ \ell\ =\ 0.46\ \ell$$

So the system will actually shrink, and the work done by the system will be negative. The amount of work will be

$$w\ =\ -P_{ext}\,\Delta V\ =\ -(26.0\ \text{atm})\ (V_{final} - V_{initial})\ =\ -(26.0\ \text{atm})(0.44_2\ \ell - 1.76_7\ \ell)\ =\ +34._{372}\ \text{atm}\cdot\ell$$

$$w\ =\ +34._{372}\ \text{atm}\cdot\ell\ \left(\frac{101.325\quad\text{kPa}}{1\quad\text{atm}}\right)\left(\frac{10^{-3}\quad\text{m}^3}{1\quad\ell}\right)\left(\frac{1\quad\text{N}\cdot\text{m}^{-2}}{1\quad\text{Pa}}\right)\left(\frac{1\quad\text{Joule}}{1\quad\text{N}\cdot\text{m}}\right) =\ +3.4_{83}\quad\text{Joules}$$

Since this change takes place at constant pressure, the heat released by the reaction will be equal to the enthalpy change, just as in the calorimetry lab. The temperature isn't exactly 25ºC, but ΔH does not have a very strong dependence on temperature provided that all the reactants and products in the standard state reaction are in the same state as in the actual reaction:

$$q\ =\ \eta_{Hydrogen}\,\Delta H^{o}_{combustion,\ hydrogen}\ =\ (1.00\ \text{mol})(-143\ \text{kJ}\cdot\text{mol}^{-1})\ =\ -286\ \text{kJ}$$

Zowie. We could make the system actually ***do*** work if we insulated the system and prevented any heat from getting out (q=0)!

That's one way of reducing the amount of energy that's released as heat, and consequently increasing the amount of work you can extract. The drawback is that to collect another "aliquot" of work, you have to cycle back to the original state of the system: and often requires an input of work, or a lot of patience. That's the challenge constantly faced by people like engine designers: they have to trade efficiency for power. A super-efficient engine is nice, but waiting 35 seconds to get from 0 to 60 mph isn't. Going from 0 to 60 mph in a few seconds with a big engine is nice, but the associated gas and environmental bill isn't.

Standard Molar Heat of Combustion ($\Delta\tilde{\mathbf{H}}_{\mathbf{c}}^{\mathbf{o}}$) – The enthalpy change per mole of a fuel associated with the following reaction (once it is properly balanced): $\text{Fuel}_{(standard\ state)} + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(\ell)}$

Note that the heat of combustion gives you the amount of heat released by burning a fuel in open air, provided that the fuel burns completely and the final products of the reaction are carbon dioxide gas and liquid water. Often real combustion processes will be incomplete (they will produce $C_{(s)}$ or $CO_{(g)}$ rather than $CO_{2(g)}$) and will produce water vapor ($H_2O_{(g)}$) rather than liquid water.

An example similar to your calorimetry lab:

Say you use methane as your reference fuel. You turn on a Bunsen burner and burn 12.4 g of $CH_{4(g)}$; this causes the temperature of your calorimeter to go up by 24.2 C°. Given the molar heat of combustion of methane is –890. kJ/mol, what is the approximate heat capacity of your calorimeter?

$$q_{fuel} = \text{Heat flow from system caused by burning fuel} = n\ \Delta H_c{}^\circ = 12.4\text{ g } CH_4 \left(\frac{1\text{ mol } CH_4}{12.01\text{ g} + 4(1.008\text{g})}\right)\left(\frac{-890.\text{ kJ}}{\text{mol } CH_4}\right) = -687._{94}\text{ kJ}$$

$$q_{calorimeter} = \text{Heat transfered into or out of the calorimeter} = C_P\ \Delta T = C_P\left(T_{final} - T_{inintial}\right) = C_P(24.2\text{ C}^\circ)$$

We make the assumption that all the heat released by burning the fuel went into heating up the calorimeter. This isn't strictly true, of course. Some of the heat released in burning the fuel escaped into the air and didn't help to heat up the calorimeter. Because of our assumption we are actually calculating an "effective" heat capacity for the calorimeter that takes into account this heat loss.

q_{fuel} is negative because burning the fuel releases heat energy to the surroundings. $q_{calorimeter}$ should be positive, because the calorimeter is getting hotter (taking in heat energy from the surroundings). Because the two systems are opposite for these two q's,

$$q_{fuel} = -q_{calorimeter} \quad \Rightarrow \quad -687._{94}\text{ kJ} = -C_P(24.2\text{ C}^\circ) \quad \Rightarrow \quad C_P = \left(\frac{687._{94}\text{kJ}}{24.2\text{ C}^\circ}\right) = 28.4\frac{\text{kJ}}{\text{C}^\circ} \quad (C_P\text{'s are always positive!})$$

Say we did two more trials and got about the same heat capacity for the calorimeter, so now we're stylin'. Now our devious prof gives us an "unknown" fuel with a molar mass of 32.04 g·mol^{-1}. We burn 27.5 g of it and the calorimeter heats up 22.7 C°:

$$q_{fuel} = -q_{calorimeter} = -C_P\ \Delta T = -\left(28.4\frac{\text{kJ}}{\text{C}^\circ}\right)(22.7\text{ C}^\circ) = -644._{68}\text{ kJ} = n_{fuel}\ \ \Delta H_c{}^\circ$$

$$\Rightarrow \quad \Delta H_c{}^\circ = \frac{-644._{68}\text{ kJ}}{n_{fuel}} = \frac{-644._{68}\text{ kJ}}{(27.5\text{ g fuel})\left(\dfrac{1\text{ mol fuel}}{32.04\text{ g fuel}}\right)} = -751\ \frac{\text{kJ}}{\text{mol fuel}} \quad \text{(This is the heat of combustion of the unknown fuel.)}$$

DeltaBuckWeights example

Δ(bw) is also an extensive state function. (bw) is the total mass of your money. Δ(bw) is the change in the mass of your money. If we live in a universe where money is conserved (you never get incorrect change), this is a pretty good analogy to ΔH. Consider:

1 dollar bill → 4 quarters Δ(bw) = + 22.8 g
\+ 4 quarters → 1 dollar bill Δ(bw) = - 22.8 g
1 dollar bill + 4 quarters → 4 quarters + 1 dollar bill Δ(bw) = + 22.8 g + (-22.8 g)

This can obviously be simplified to no net change in anything…if you trade your dollar bill in for four quarters, then trade your four quarters back in for a dollar bill, there is no net change in either the identity of the money in your pocket or its total mass. But…

1 dollar bill → 4 quarters Δ(bw) = + 22.8 g
\+ 4 quarters → 10 dimes Δ(bw) = + 0.2 g
1 dollar bill + 4 quarters → 4 quarters + 10 dimes Δ(bw) = + 22.8 g + (+0.2 g)

Canceling the four quarters that appear as both reactants and products in the reaction above, we get the net reaction

1 dollar bill → 10 dimes Δ(bw) = + 23.0 g

Guess what? That's exactly the end result of either trading in a buck for ten dimes, or trading in a buck for four quarters which you then trade in for ten dimes. You end up with ten dimes and nothing else, and your pocket weighs 23.0 grams more than it did before you started the entire process. Let's get tricky:

1 dollar bill → 4 quarters Δ(bw) = + 22.8 g
1 quarter → 2 dimes + 1 nickel Δ(bw) = + 3.9 g
1 quarter → 2 dimes + 1 nickel Δ(bw) = + 3.9 g
1 quarter → 2 dimes + 1 nickel Δ(bw) = + 3.9 g
\+ 1 quarter → 2 dimes + 1 nickel Δ(bw) = + 3.9 g
1 dollar bill + 4 quarters → 4 quarters + 8 dimes + 4 nickels Δ(bw) = (+ 22.8 g) + (+3.9 g) + (+3.9 g) + (+3.9 g) + (+3.9g)

Canceling out terms that appear on both sides of the net reaction, we get

1 dollar bill → 8 dimes + 4 nickels Δ(bw) = + 38.4 g

A shorter way of writing this same thing would be (note that we have to multiply Δ(bw) by four as well, it is an extensive property):

1 dollar bill → 4 quarters Δ(bw) = + 22.8 g
\+ 4 (1quarter → 2 dimes + 1 nickel Δ(bw) = + 3.9 g)
1 dollar bill + 4 quarters → 4 quarters + 8 dimes + 4 nickels Δ(bw) = (+ 22.8 g) + 4 (+3.9 g)

This simplifies to give the same net result as the calculation above.