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HOT PADS AND COLD PADS

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HOT PADS AND COLD PADS

Hot/cold packs are handy items designed to provide local heat/cold. Main application is therapeutic (to alleviate pain), with desired temperatures of just above body-temperature (say 38 °C) for heat-therapy, and just above freezing (say 1 °C) for cold-therapy.

Hot pads must be exothermic, $dH < 0$, and cold pads endothermic, $dH > 0$. But for the evolution of any un-powered system, its Gibbs function, $dG = dH - TdS < 0$, i.e. must decrease, teaching that exothermic processes are easier to realise than endothermic processes, for which a large increase in entropy is required to overcome the enthalpy increase.

We only consider here autonomous systems, i.e. the first group in the following device classification:

- Autonomous systems. Carried along at ambient temperature and ready to yield heat/cold at the desired time (on trigger by a squeeze) due to a physicochemical reaction (mixing, oxidation).
- Depending systems. Provide heat/cold only after being removed from a freezer/heater. A high-heat-capacity substance or a phase-change material is used, as in traditional water-bags for heating (also bricks, waxes, and silica packs are used), and the traditional ice-cubes for cooling (also encapsulated gels are used). The most convenient hot-substances are microwaveable. Notice that, if appropriate adiabatic containers were available, the entire system would become an autonomous system, to be started at the desired time by removing the adiabatic wall.
- Wired systems, which only provide heat /cold when electrically powered by the mains, as in the traditional pillow-heater.

HOT PADS

Hand warmers (also known as heat/hot pads/pouches/compresses) are small energy stores for effective and controllable heat release for topical applications (Table 1). Systems based on the enthalpy of phase-change, mixing or oxidation, compare most favourably to other possible solutions.

Table 1. Hand warmer characterisation.

<i>Characteristics</i>	<i>Comments</i>
Small	From 0.1 kg to 1 kg and less than 1 dm ³ .
Safe	< 50 °C (not pyrotechnic), non-toxic.
Cheap	It depends, but ≈1 € if disposable.
Effective	High instant energy release, anywhere, at anytime.
Controllable	Easy start and long lasting (there is no need of controllable stop).
Applications	Therapeutics (arthritis pain, back pain, sore neck), winter sports, outdoors (camping, fishing, parades), food warming (baby bottles).
Types	<ul style="list-style-type: none"> • Reversible (reusable by simple means): solidification enthalpy. • Disposable or irreversible (too expensive to regenerate): mixing enthalpy, oxidation enthalpy.
Energy intensity	Thermophysical systems have 100..300 kJ/kg. Mechanical systems have <10 kJ/kg (compressed air, springs). Electrochemical system give >100 kJ/kg but are expensive and massive (batteries). Fuels are powerful (50 MJ/kg _{fuel} , 500 kJ/kg for a 0,1 kg appliance) but unsafe to ignite (spark), and unsafe to handle (high temperatures, burning exhaust, air intake).

REVERSIBLE TYPES

Reversible hot/cold packs can be reused many times after proper simple regeneration (i.e. reheating, recooling, winding up, but remember we only consider autonomous declanchable systems, not simple preheated or precooled systems). Mixing is not considered reversible because demixing is not an easy task, but melting-solidification is considered reversible.

Three types of solidification processes can be distinguished: from the melt, from solution and from the vapour. The latter is not good for energy storage purposes because of the low density of the vapour. From a practical point-of-view, phase-change-materials (PCM) used to store energy are grouped as:

- Hydrated salts (i.e. solid compounds containing definite amounts of bounded water), the most popular being Glauber's salt (sodium sulphate decahydrate, Na₂SO₄·10H₂O). Others are: calcium chloride hexahydrate (CaCl₂·6H₂O), magnesium chloride hexahydrate (MgCl₂·6H₂O), and magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O).
- Waxes and other organic compounds (e.g. pentacosane, C₂₅H₅₂, T_m=54 °C, derived from beewax; hexacosane, C₂₆H₅₄, T_m=57 °C, derived from methane).
- Other inorganic compounds (e.g. low-melting-point metals).

Salts are widely used as PCM because they are cheaper, although they present some problems: they are more aggressive to the container material, they decompose after many cycles, and they show large undercooling. The latter, a nuisance for energy storage, is of the greatest interest to our present application of hot pads. Indeed, a simple reversible system like a salt that would solidify below 15 °C and would melt above 15 °C, is not very useful for the purpose of hot/cold pads: it would release heat/cold if the ambient temperature falls/rises below/above 15 °C, but not at our will. A hysteretic system is needed with sufficient undercooling/overheating capability not to be de-clinched under foreseeable ambient-temperature variations, but at our command, that is why the only practical process developed has been a solidification device based on hydrated-salt crystallisation.

Solidification of hydrates

The usual type of hot pad is a sodium-acetate solution aqueous solution (half and half salt and water in weight), in metastable equilibrium at ambient temperatures (say 0..40 °C) and pressure (adding a small crystal would trigger the phase change in a few seconds). A typical heat pad is a thin, flexible, vinyl plastic pouch say 0.1 m in side, and some 0.01 m in total thickness. Similar behaviour to sodium acetate is shown by other salts, as sodium sulphate (Na₂SO₄) and sodium thiosulphate (Na₂S₂O₃), but they are not used.

Pure anhydrous sodium acetate (NaC₂H₃O₂, or CH₃COONa, or NaA for short) is a water-soluble food-grade white powder salt, with $M=0.082$ kg/mol, $\rho=1530$ kg/m³, melting at $T_m=324$ °C ($h_{SL}=250$ kJ/kg, $c_S=2200$ J/(kg·K), $c_L=3600$ J/(kg·K)), decomposing at $T_b>400$ °C, pH=8..10, water solubility 470 g/L at 0 °C, is obtained from acetic acid and sodium hydroxide by thermal dehydration. It is a white or transparent hygroscopic crystalline powder when solid, transparent when molten, sometimes used as road de-icing (less harmful than NaCl, but more expensive) and as mordant in dyeing.

Sodium acetate forms a hydrate compound with water: sodium acetate trihydrate (NaC₂H₃O₂·3H₂O(s), NaAT for short) with $M=0.136$ kg/mol, $\rho=1450$ kg/m³, water solubility 760 g/L at 0 °C, pH=9, thawing at $T_s=54$ °C, melting at $T_s=120$ °C and decomposing at $T_s>300$ °C. Both, NaA and NaAT are partially soluble in water, yielding sodium and acetate ions, with a small mixing enthalpy (the heat of solution of NaAT is 19.7 kJ/mole, i.e. endothermic, contrary to the crystallization of NaAT that is highly exothermic).

The flexible plastic pouch contains nearly equal amounts of dehydrated salt and water. Well above the crystallisation point of NaAT (e.g. at >60 °C), there is a transparent liquid inside the plastic pouch: a NaA and NaAT solution. But when temperature falls below NaAT-solidification point (e.g. at 0..40 °C), a subcooled-liquid remains, supersaturated with respect to NaAT (but unsaturated with respect to NaA). This kind of metastable equilibrium is common in viscous materials with complex molecules; it is difficult for these particles to organize themselves and they do not simply freeze at a sharp temperature like water, but form subcooled liquids, gels or glasses. Nucleation is not easy, small perturbations are not effective, but a crystal seed or a pressure-pulse from a small metallic clicker inside can trigger it (causes small cavitation bubbles), and the solidification of NaAT starts (it lasts some seconds), releasing the solidification enthalpy:



When solid-NaAT is heated well above its crystallisation point, it releases its water of hydration and begins to dissolve in that water (it completely dissolved when the mixture reaches 79 °C, the temperature at which a saturated solution of anhydrous sodium acetate has the same composition as the trihydrate).

It is better to store pouches in subcooled liquid form, since water loss through the vinyl enclosure is larger when the salt is crystallised (what might give rise to some snowflake-like white-crystals in the

supersaturated liquid. This evaporation can be reversed by immersing the pad in simmering water for extended periods and leaving it in the water to cool.

Pros: Reversible (by <10 minutes reheating at more than 80 °C, e.g. on boiling water, but not in a microwave).

Cheap (5 € a 0.12 kg, 0.1x0.1 m² plastic pouch).

Energetic (some 50 W at 54 °C for up to 30 minutes, depending on size, starting temperature and insulation).

Easy trigger by a pressure pulse with a clicking of a stainless steel disc (a clicker or cricket).

Cons: Subcooled liquid only for $T_{\text{amb}} > -5$ °C.

May slowly freeze or started unadvertedly.

Low energy content (150 kJ/kg).

Uncontrollable release rate (nucleation controlled).

Hazard if pouch breaks (may be irritating to the respiratory tract, skin and eyes), and flammable.

Ref.: <http://www.hotpadz.com/>, <http://thermo-pad.com/>,

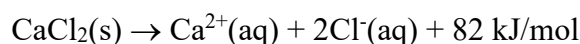
IRREVERSIBLE TYPES

Mixture enthalpy

Real mixtures show an enthalpy of mixing, positive (endothermic) or negative (exothermic) but usually of a small value. Most mixtures are mildly exothermic (e.g. alcohol and water) for entropy reasons, as explained above. Sometimes special names are given to mixing enthalpy according to the guest phase (heat of absorption, heat of solution).

Real mixtures also show a small volume change when mixing. It frequently happens that mixtures with exothermic heats of mixing expand (e.g. water and alcohol; mixing roughly equal parts of acetone and chloroform produces a decrease in volume of about 0.2%), while mixtures with endothermic heats of mixing tend to contract.

The usual mixture for hot pads is water with anhydrous calcium chloride salt (CaCl_2 , $M=0.147$ kg/mol), initially isolated in an inner ampoule. The reaction when it breaks is:



The driving force is the hydration enthalpy, with negligible entropy contribution. Indeed, from this point of view, the reaction is the formation of the monohydrate, dihydrate and hexahydrate; e.g.:



Pros: More energetic (60 W at 50 °C for 10 minutes).

Cheap reactives.

Controllable release rate (but difficult in practice: mixing controlled).

Easy trigger (by breaking a barrier).

Cons:Not reusable.

Other exothermic mixtures, not used for this application, are:

- Water and anhydrous magnesium sulphate salt (MgSO_4 , $M=0.246$ kg).
- Water and a concentrated acid (e.g. sulphuric acid; see Notes below).
- Water and sodium hydroxide pellets (NaOH , see Note 3 below).
- Water and quicklime (calcium oxide, CaO).

Note 1. Why acid and water mixtures are exothermic

If you look at the equation for dissolving a strong acid like HCl in water, $\text{HCl} + \text{H}_2\text{O} = \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$, you might think at first that this would have to be a heat-absorbing (endothermic) process, because it looks like the bond between H and Cl is broken. But there is another reaction hiding here: the hydrogen ion reacts with water to form a complex of the form $(\text{H}_2\text{O})_n \cdot (\text{H}_3\text{O})^+$; it is this hydration process that releases the energy.

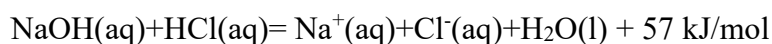
Concentrated sulphuric acid (H_2SO_4) is used to dehydrate sugar in a classic (and dangerous) demonstration where a sugar-box (sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is dehydrated to carbon and water. The water produced by the sugar hydrates the sulphuric acid. The formation of strong hydrogen bonds between the acid and the water makes the process exothermic enough to vaporize the hydrated sulphuric acid.

Note 2. Why is acid always added to water, and not the reverse

A large amount of heat is released when acids are mixed with water; the stronger the acid, the stronger the heat. So, if you add water to concentrated acid, you form an extremely concentrated solution of acid locally, and so much heat is released that the solution may boil violently, splashing concentrated acid out of the container. If you add acid to water, the solution that forms is very dilute and the small amount of heat released is not enough to vaporize and sputter it.

Note 3. Why alkali and water mixtures are exothermic

For the same reason as for acids (see Note 1). An extreme example of an exothermic heat of mixing is provided by adding an aqueous solution of sodium hydroxide, a powerful base, to an aqueous solution of hydrogen chloride, a powerful acid; the hydroxide ions (OH^-) of the base combine with the hydrogen ions of the acid to form water, a highly exothermic reaction:

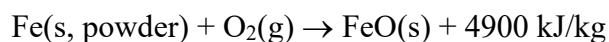


Oxidation enthalpy

Similarly to mixtures, most oxidative processes are exothermic (e.g. combustion), but the enthalpy change is much larger than for mixtures.

The usual reactive is iron powder. It is the reverse of iron ore (iron oxide) conversion in the blast furnace, what requires tremendous amounts of heat energy. When iron spontaneously oxidizes back to iron oxide (rust) in the air the heat released is not noticeable; but when this reaction is sped up, the amount of heat is

noticeable and usable in the form of a hand-warmer (they were introduced by the Japanese in 1978). They usually require a catalysts (a water-charcoal-salt-cellulose gel for iron oxide).



The content is iron powder, water, salt, activated charcoal and cellulose in a cloth-bag enclosed on a plastic bag to keep moisture away before use (the cloth-bag may be substituted by a polypropylene bag that is permeable to air but impervious to water).

Pros: The most energetic (60 W at 60 °C for >6 hours; the maximum heat of the product and the length of the reaction can be very tightly controlled by the chemical formulation and the amount of air allowed in the warmer).

Easily controllable release rate (aeration controlled).

Easy trigger (by unfolding).

Cons: Not reusable.

Expensive.

Porous pouch (may leak).

Ref.: <http://www.grabberwarmers.com/>.

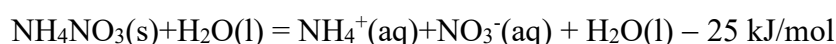
More energetic is a composite of magnesium and iron powders inside a resistant bag; when water is added, the reaction gets hot enough for the water to boil (used to heat meals by army or trekking people).

Other exothermic reactions, not used for this purpose, is the neutralising of a strong acid solution with a strong alkali solution, as for HCl(aq) plus NaOH(aq).

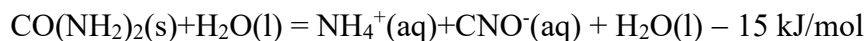
COLD PADS

There are substances that cool when mixing, but usually not enough for practical application (e.g. both, sugar and salt dissolve in water endothermically (i.e. slightly cooling in a calorimeter, or absorbing some heat from the environment), but there are certain substances that produce enough cooling effect to be used in medicine and sport as cold pads (also known as ice packs)..

The most popular cold pad is a plastic bag filled with water, inside which there is an ampoule of ammonium nitrate (NH₄NO₃, a white granulated solid used in fertilisers and explosives). Breaking the inner barrier causes the endothermic dilution:



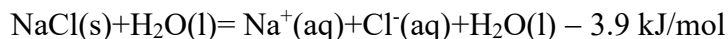
to take place, quickly (in less than a minute) lowering the system temperature to near 0 °C for some 10 minutes (depending on size). For adiabatic mixing, the temperature drop is quasi-linear with concentration, roughly -5.4 °C/(mol/dm³). A less powerful solution uses urea crystals instead of ammonium nitrate:



though some cyanate ions (CNO^-) may further decompose to CO_2 and NH_3 .

Other endothermic mixtures, although not used for this application are:

- Water and common salt:

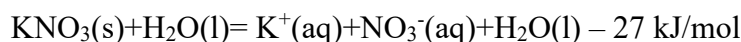


This is a small enthalpy change, of little practical use; it is the mixture of salt with ice that is highly endothermic because of the melting enthalpy of water, what is commonly used in road de-icing.

- Water and sodium nitrate salt:



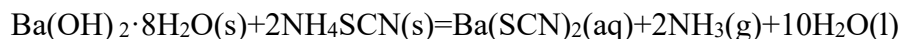
- Water and potassium nitrate salt the temperature drop is quasi-linear with concentration, roughly $-6.9 \text{ }^\circ\text{C}/(\text{mol}/\text{dm}^3)$:



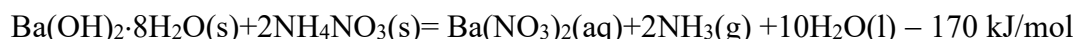
- Water and ammonium chloride (dissolving 30 g of salt in 100 g of water at $15 \text{ }^\circ\text{C}$ adiabatically lowers the temperature to $-5 \text{ }^\circ\text{C}$).



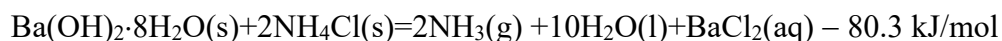
- Hydrated barium hydroxide and ammonium salts are more endothermic, the most endothermic being ammonium-thiocyanate salt (when they react, the products dissolve in the hydration water):



- Hydrated barium hydroxide octahydrate with ammonium nitrate:



- Hydrated barium hydroxide octahydrate with ammonium chloride:



A popular demonstration is to freeze water by mixing the two crystalline substances together in a beaker and then setting it onto a puddle of water, on a wooden board; in a couple of minutes the flask and the board are frozen solidly together (some 40 °C drop); the odour of ammonia is felt if the flask is opened.

Notice that for a process to proceed naturally (i.e. without adding exergy), Gibbs's function change for the process has to be negative; e.g. for the cold pad made with hydrated barium hydroxide octahydrate and ammonium chloride, $h_r^\oplus=80.3$ kJ/mol, $s_r^\oplus=428$ J/(mol·K), and consequently $g_r^\oplus=h_r^\oplus-T^\oplus s_r^\oplus=80.3-0.298\cdot 428=-47$ kJ/mol (negative, as expected).

COMPARISON OF HOT / COLD PROCESSES

Table 2 in Solutions gives heat-of-solution values for many substances; those with positive values (e.g. NaCl or NH₄NO₃) yield endothermic mixing and produce cold, whereas those with negative values (e.g. CaCl₂ or sugar) yield exothermic mixing and produce heat. Table 2 presents a more general summary of hot / cold processes.

Table 2. Comparison of hot / cold processes.

<i>Exothermic processes</i>	<i>Endothermic processes</i>
Phase change: - making ice cubes (heat must be removed) - formation of snow in clouds - condensation of rain from water vapour - crystallizing liquid salts (e.g. sodium acetate)	- melting ice cubes (heat is absorbed) - conversion of frost to water vapour - evaporation of water - making an anhydrous salt from a hydrate
Mixing: - forming ion pairs - mixing water with most salts (e.g. CaCl ₂) - mixing water and strong acids - mixing water and strong alkali	- separating ion pairs - mixing water with some salts (e.g. NH ₄ Cl) - -
Oxidation: - a candle flame - rusting iron - burning sugar	- fuel synthesis - producing iron from its ores - producing a sugar by photosynthesis
Other: - joining atoms to make a gas molecule - nuclear fission	- splitting a gas molecule apart -

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