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### THERMAL EFFECTS IN RADIATION PROCESSING

Z. P. Zagórski\*

Radiation Laboratory  
University of Notre Dame  
Notre Dame, IN 46556 U.S.A.

**MASTER**

\* On leave of absence from the Institute of Nuclear Chemistry and Technology, Warsaw, Poland.

*Jaw*

## ABSTRACT

The balance of ionizing radiation energy incident on an object being processed is discussed in terms of energy losses, influencing the amount really absorbed. To obtain the amount of heat produced, the absorbed energy is corrected for the change in internal energy of the system and for the heat effect of secondary reactions developing after the initiation. The temperature of a processed object results from the heat evolved and from the specific heat of the material comprising the object. The  $c_p$  of most materials is usually much lower than that of aqueous systems and therefore temperatures after irradiation are higher. The role of low specific heat in radiation processing at cryogenic conditions is stressed. Adiabatic conditions of accelerator irradiation are contrasted with the steady state thermal conditions prevailing in large gamma sources. Among specific questions discussed in the last part of the paper are: intermediate and final temperature of composite materials, measurement of real thermal effects in situ, neutralization of undesired warming experienced during radiation processing, processing at temperatures other than ambient and administration of very high doses of radiation.

## KEY WORDS

adiabatic irradiation, cobalt 60 source, cryogenic irradiations, electron accelerator, low temperature processing, radiation chemistry, radiation processing, radiation sterilization, thermal effects of irradiation, thermochemistry of irradiation.

## 1. INTRODUCTION

The nature of radiation processing consists of energy delivery from the outside into an object. This operation would apparently be similar to heating, were it not for the fact that ionizing radiation is a form of energy which is able to create chemical changes in the exposed material at or below room temperature. The heat applied in small doses in such conditions seldom induces a chemical change, although it modifies the rate of chemical reactions. However, ionizing radiation changes materials even at liquid helium temperatures, creating very reactive species. These species may be formed by heat only at elevated temperatures of thousands of degrees Celcius.

Creation of new species, both intermediate and stable, changes the internal energy of the material. The basic consideration of energetics in radiation processing is the energy balance. Therefore the first part of this paper is devoted to a qualitative treatment of the participation of particular secondary forms of energy. Energy flow diagrams will be presented for typical cases - from negligible participation of chemical energy to the cases of chemical energy released by ionizing radiation and dominating over the energy supplied from the outside.

The second part of the paper is devoted to the calculation of the resulting temperature of an irradiated object. This effect is governed by the specific heat of the object or of its parts as in the case of a composite (heterogeneous) structure.

The last part of the paper describes different aspects of

the energy balance and the resulting temperature changes which are interesting to the practice of radiation processing.

## 2. THE ENERGY BALANCE OF IRRADIATED OBJECTS

There are several sources of outside energy which may be supplied to an object, without "touching" it, i.e. not like a stream of hot gases does. These are electromagnetic radiations belonging to different parts of the spectrum and fast particles like accelerated electrons. Mentioning only these which are useful for processing and starting with lowest quanta of energies (longest wavelengths) one has: microwaves (e.g. microwave oven), infrared radiation (e.g. hot wire irradiators), visible light (e.g. xenon arc lamps), ultraviolet light (e.g. UV-curing "black light" lamps), ionizing radiation (e.g. gamma from cobalt 60) and finally subatomic particles which are accelerated to high speeds, achieving sufficient penetration and the capacity of produce ionizations. The initial, physical stages of absorption of these high energy radiations, have in common the fact that the incident radiation is not deposited in the object fully, but is partially lost. In the case of lower energy radiations, e.g. IR-VIZ-UV reflection from the target object is important. In ionizing radiations, reflections (albedo) are small but another mechanism of losing energy is important, i.e. the secondary high energy radiation powerful enough to leave the object. Secondary radiation whose penetrating power exceeds that of the original beam is particularly important to accelerated electron irradiation (bremsstrahlung). To finish with the initial phase of deposition

of energy one has to mention, that in many cases of radiation processing most of the incident radiation is transmitted through target materials.

Figure 1 shows the basic initial energy balance schematically. The partition between nonabsorbed and absorbed incident energy depends on the physical properties of the object and its shape. It is evident that even when an object is placed into hitherto well known irradiation environment, no precise description of the energy absorbed can be assumed. Only proper dosimetry, matched both to the type of irradiation and to the object may give the answer.

One has to remark that all considerations about the energetics of irradiated systems concern themselves with chemical changes, i.e. those in which only outer shell electrons are changing location. Therefore the sorts of radiation which may cause nuclear activation are not considered (nuclear reactor radiation containing neutrons, heavy particle beams of high energy, etc.). Electron beam radiation and X rays of energy above 13 MeV (tails of energy distribution included) may cause photoactivation, disturbing the early and transient thermal picture and the general energetics.

The net energy absorbed by the object undergoes further transformations in next events. The fate of absorbed energy is simple in materials which do not undergo chemical changes. For instance, in metals, atoms are ionized in concentration proportional to the dose rate. The new electrons increase the population of already existing electrons. Therefore the internal energy

of the system changes only temporarily. All electronic changes come back to normal very quickly and the concentration of permanent displacements caused by very few elastic collisions may be neglected. The system comes back to normal and the supplied energy appears as increased vibrations of the lattice or of movements of atoms (in the case of irradiated liquid metals).

The absorbed energy may be expressed in any units of energy: according to the SI system - in joules referred to the unit of mass as greys ( $1\text{Gy} = \text{J/kg}$ ). In older units, but still familiar to us, the absorbed energy is expressed in rads ( $100 \text{ erg/g}$ ) and recalculated to old, but easy to visualise calories,  $1 \text{ Mrad} = 2.389 \text{ cal/g}$ .

If new chemical compounds are formed as a result of irradiation, changes will occur in the thermal effect. The thermal effect may be smaller (formation of compounds of higher internal energy) or larger (formation of compounds of lower internal energy). One of the well known systems, the ferrous-ferric couple in 0.8 N sulphuric acid (Fricke dosimeter), became a classic illustration of these two possibilities. In a slightly simplified textbook example (Henglein, 1) one can find that the reaction in the presence of oxygen runs exothermically (enthalpy of reaction  $\Delta H = -21.9 \text{ kcal mole}^{-1}$ ). i.e. for the every 100 eV of supplied energy,  $G \times \Delta H/23.06 = 14.7 \text{ eV}$  of additional heat is released. In a deaerated system the reaction of  $\text{Fe}^{2+}$  oxidation is endothermic (enthalpy of reactions  $\Delta H = 12.3 \text{ kcal} \times \text{mole}^{-1}$ ) i.e. for every 100 eV of energy supplied,  $G \times \Delta H/23.06 = 4.3 \text{ eV}$  of energy will go into internal energy of the system. Therefore

the oxygenated system produces 14.7% more heat and the deaerated one 4.3% less heat than the net physically deposited energy would have produced.

In the case of a chain reaction, the participation of internal energy changes will be dramatically higher. A thoroughly investigated inorganic chain reaction in aqueous solution is an example. The reaction  $2 \text{SO}_3^{2-} + \text{O}_2 \rightarrow 2 \text{SO}_4^{2-}$  in alkaline solution (2) is very slow without a catalyst. However, the system (1 M NaOH, 20 mM  $\text{SO}_3^{2-}$ , 0.5 mM  $\text{O}_2$ ) in gamma radiation consumes oxygen with  $G_{\text{O}_2} = 1000$ . In electron pulse irradiation (5 Gy delivered in a 0.5  $\mu\text{s}$  pulse) the yield is  $G_{\text{O}_2} = 505$ . As the reaction is exothermic ( $\Delta H = -135 \text{ kcal} \times \text{mole}^{-1}$ ), for every 100 eV of energy supplied,  $G \times \Delta H / 23.06 = 2956$  eV of energy is evolved as heat. This means that in a one 0.5 krad pulse 0.0372 calories of heat is evolved as opposed to the caloric equivalent of the absorbed dose which is only .00119 cal. It is not dangerous to the system, because the concentration of reagents is low and subsequent pulses are causing a complete removal of oxygen. The situation looks different in polymerizing systems where the whole object is reacting and the heat evolved may bring the mixture to the boiling point. New reactions of degradation start to dominate.

The approach to thermal calculations is simple. One does not need to take into account that the reacting system goes through intermediate stages of higher internal energy versus the initial or final components of the system. As in all thermochemical calculations (Hess law) only the initial and the final state

of internal energy is analyzed. The calculations are done conventionally. The method of calculation is not important. For instance, sulphite ion oxidation mentioned above gave for  $\Delta H$  the value (in kcal/mole) of -134.6 from the heat of ion formation, -133.2 from the free energy and the entropy of ions, and -136.6 from the hypothetical electrochemical cell. These unimportant variations result from differences in basic values occurring in tables and from different measurement errors.

Heats of reactions induced by radiation in polymerizing or crosslinking systems are calculated similarly, without regard that between the starting and final state an irradiation took place. One has to remember that in contrast to the low yield processes which exhibit a negligible energy of activation (low temperature coefficient), the secondary chain reactions usually show a pronounced dependence on temperature (see part 4 or the paper).

Figure 2 depicts the energy balance, starting with net absorbed energy shown on Fig. 1. The time scale of events is of interest for a specialist in radiation processing. Deposition and transformations of energy described in Fig. 1, sometimes called a physical stage of absorption of energy, occur very rapidly, i.e. are finished already 1 ps after the ionizing particle or photon has interacted with the object. Next events, chemical ones, are slower but still fast in comparison with the rate of passing the object under the scanned electron beam. These reactions are complete within microseconds (e.g. free radical oxidation of  $\text{Fe}^{2+}$ , Fig. 2) or milliseconds (oxidation of

sulphite, Fig. 2) and can be investigated by pulse radiolysis. Other reactions, e.g. additional oxidation of  $\text{Fe}^{2+}$  by  $\text{H}_2\text{O}_2$  takes minutes and can be followed already in a gamma irradiation experiment. In systems solid at room temperature and frozen ones, the completion of reaction may take place even after a much longer time, and the release of final portion of heat may be observed long after the irradiation.

### 3. FINAL TEMPERATURE OF IRRADIATED OBJECT

Whatever the source of thermal energy in irradiated object - either the net energy of absorbed radiation or the additional energy released as the result of a chemical reaction, the final temperature of the irradiated object depends on its specific heat. Once the energy evolved is calculated in calories and if the irradiated object consists mainly of water, the increase of temperature may be estimated roughly without calculation. The temperature difference in  $\Delta$  K is fortunately numerically equivalent to the energy expressed in calories per gram of substance with unity specific heat. Thus 1 Mrad which is equal to 2.389 cal/g causes an increase of temperature by  $\Delta$  2.389K, if no chemical reaction is involved.

Water shows a high specific and therefore such a uniquely low increase of temperature. Almost all other materials including ice ( $\text{H}_2\text{O}$ ) have much lower specific heats and thus higher increases of temperature. Table 1 gives an idea about the variety of specific heats ( $c_p$ ) of different materials. Authors of early papers (3,4) dealing with the thermal effects in

radiation processing were assuming that the heat capacity of most polymers is  $0.4 \pm 0.1 \text{ cal g}^{-1} \text{K}^{-1}$ . If one considers also the  $c_p$  at other temperatures (both lower and higher than the ambient), the differences between particular polymers and all materials in general, become even larger than expected. The expected increase of temperature is calculated, due to a dose of 1 or 3 Mrad (10 or 30 k Gy) of ionizing radiation delivered to these materials under adiabatic conditions (high power accelerator irradiation). Under "adiabatic irradiation", an operation is assumed in which the target received the entire dose in a time too short to permit a significant exchange of heat with the environment.

Table 1 serves only as a preliminary approach to the problem and in developing a new technology, the radiation processing specialist has to turn to the literature to find the specific heat of the system most close to his own. Unfortunately, due to the gradual switch to the SI system, different units and terms coexist even in the most recent publications (e.g. 5). To avoid mistakes in calculations in the present transition period, one has to remember that heat capacity is understood to be the quantity of heat which is required to increase the temperature of a substance of a system by one degree ( $\Delta 1\text{K}$ ). It is expressed in calories per gram and degree (cal/g K) or, according to SI in joules per gram and degree (J/g K). Specific heat is the ratio of thermal capacity of a substance to that of water at  $15^\circ\text{C}$ . Dimension is unity and is numerically equivalent to the heat capacity if the latter is expressed in  $\text{cal g}^{-1} \text{K}^{-1}$ . The molar heat capacity is the quantity of heat necessary to raise the

temperature of one molecular weight (gram mole) of the substance by one degree ( $\text{J mol}^{-1} \text{K}^{-1}$ ). Unfortunately, the "heat capacity" (without "molar") is understood sometimes as molar heat capacity. In the case of polymers the weight of the repeating unit (formula weight) is taken as the molecular weight. For example, amorphous polystyrene has the molar heat capacity  $c_p = 122.6 \text{ J mol}^{-1} \text{K}^{-1}$ , or,  $c_p = 122.6/104.15 = 1.177 \text{ J g}^{-1} \text{K}^{-1}$ , or,  $c_p = 1.177 \times 0.239 = 0.281 \text{ cal g}^{-1} \text{K}^{-1}$  (at 290 K).

All varieties of heat capacity of solids and liquids are designated by  $c_p$  i.e. under constant pressure, unless otherwise specified.

As the heat capacity is the key macroscopic material property, from which other thermodynamic functions, enthalpy, entropy and Gibbs energy can be derived, many groups of researchers redetermine the old values, using better methods and better defined materials. It is advisable to look for the newest, critical data, because they may differ substantially from the older ones. Unfortunately, only few really critical compilations are available, which, after careful analysis recommend selected values as best ones. For radiation processing of polymers, a series of papers entitled "Heat capacity and other thermodynamic properties of linear macromolecules" by Gaur et al. (from Part I, to Part VIII, 6) is of much value.

The best data found in the literature refer to pure materials of research quality and definition, rather than to technical grade polymers, copolymers and compositions, used in radiation processing, sterilization, etc. The most scattered data are

found on PVC which is particularly diversified containing a variety of additives which strongly influence the heat capacity. The recommended values of  $c_p$  for reasonably pure, amorphous poly(vinyl chloride) is, at 290K  $c_p = 57.64 \text{ J mol}^{-1} \text{ K}^{-1}$  (7);  $c_p = 1.10 \text{ J g}^{-1} \text{ K}^{-1}$ ;  $c_p = 0.263 \text{ cal g}^{-1} \text{ K}^{-1}$ . Papers by Dunlap (8) on the specific heats of PVC compositions ( $c_p$  is important for the purpose of extrusion) show that additives have a pronounced influence on the specific heat. For instance, the addition of barium-cadmium stabilizer lowers, as expected, the  $c_p$  at 300 K from 0.270 (pure material) to 0.223  $\text{cal g}^{-1} \text{ K}^{-1}$  and the addition of dibutyltin dithioglycollate, a plasticizing stabilizer, lowers it to 0.235. On the other hand, an addition of the plasticizer di-2-ethylhexyl azelate (30 phr) increases the  $c_p$  to 0.354.

If the value of  $c_p$  has not been needed for a particular composition of material, there is little chance that the value can be found in the literature. Special attention is advised if heavy metals (e.g. as organometallic compounds) are incorporated, they will lower the specific heat. Addition of finely divided compounds, like  $\text{Sb}_2\text{O}_3$  as flame retardant in amount of up to 50% changes very much the heat capacity in unfavorable direction. As the temperature reached after irradiation may be critical, it is recommended to measure this property precisely enough. Many methods are available. DSC is widely available and dependable.

Heat capacity shows pronounced dependence on temperature. At 0 K, or close to it,  $c_p$  is almost zero in the case of crystalline materials and from that point on it rises in a mode indi-

cating differences in the structure of the material (e.g. between amorphous and crystalline). Simple dividing of energy evolved, expressed in calories per gram, by the specific heat (in calories per gram and kelvin) in calculation of the temperature rise, is precise enough only if the dose is low and the specific heat high. Otherwise one has to analyze the change of  $c_p$  in the function of temperature above the starting temperature. Usually the increase may be assumed to be a linear one in the part of the temperature range and the slope  $a$  (in  $\text{cal g}^{-1} \text{K}^{-2}$ ) has to be determined. The increase of temperature ( $X$ ) will be  $aX^2 + 2c_p X - D = 0$  where  $c_p$  is heat capacity at the start of irradiation ( $\text{cal g}^{-1} \text{K}^{-1}$ ) and  $D$  dose (in  $\text{cal g}^{-1}$ ). The quadratic solution is

$$X = \frac{\sqrt{4 c_p^2 + 8 Da} - 2c_p}{2a}$$

Values of  $\Delta T$ , in Table 1 has been calculated in this way if proper basic data were available. If a change takes place during irradiation or  $c_p = f(T)$  has complications, more complex calculations are needed, e.g. by separation of the  $c_p$  vs.  $T$  curve into zones of almost linear dependence.

Some examples of low temperature heat capacities are shown in Table 1. They help to visualize that as water crystallizes into ice the  $c_p$  drops abruptly to 50% and in liquid nitrogen to 16.2% of its value for water at  $0^\circ\text{C}$ . This means that one megarad causes an increase of temperature by  $\Delta 13.5 \text{ K}$  - in ice ( $\text{H}_2\text{O}$ ) at  $77\text{K}$ , a fact which is not always realized in low temperature processing. Calculations of temperature rise at cryogenic irradiation

tions must take into account the change of specific heat with the temperature, especially at high doses. Thus, application of 3 Mrad to ice (water) of starting temperature of 77K would give  $\Delta$  44.2 K, assuming  $c_p$  value of 0.162 throughout the operation. Due to the change of  $c_p$ , the increase of temperature will be  $\Delta$  28.0 K. Figure 3 provides an estimate of the error if the change in  $c_p$  during irradiation is not taken into account. The error increases at low temperatures, and is already pronounced in liquid nitrogen irradiation data.

The situation at liquid helium temperature (4K) is even more dramatic and provokes the question, "Really how cold is low temperature radiation chemistry?". Extremely low temperature irradiation is presently outside the interest of the main stream of radiation processing, but there are indications that it will soon be important in the processing of semiconductor materials. Until now radiation chemistry at liquid helium temperature was a field explored by basic researchers only. For some time the high jump of temperature in irradiated materials was not realized, but now it is beginning to be considered. Extremely low temperature experiments are performed mainly with pulse radiolysis at low doses. In recent years, researchers became aware of the temperature jump. Kawabata, Buxton and Salmon (9) estimated that a 5 krad pulse raises the temperature of an  $H_2O$ -ice from 6K to 13K. Others estimate differ substantially. For instance, Van Leeuwen, Heijman, Nauta and Casteleijn (10) were using 2 MeV electrons in pulses of 0.55  $\mu$ s duration, delivering doses of 3-5 krad (30-50 Gy) to frozen 8 M NaOH glass under liquid helium.

Assuming value of  $c_p$  based on data for similar materials (the heat capacity of the sample was now known), the authors have estimated that the average rise in temperature caused by the electron pulse at 10 K does not exceed  $\Delta 3$  K. However, the temperature relations in such irradiations demand further study. As the authors remark: "Because the energy dissipation occurs mainly in the spurs, the local rise of temperature will be much larger, than  $\Delta 3$  K. It is not known what effect this will have on the formation of trapped electrons". In conclusion one can say, that if the true increase of temperature in low temperature radiation chemistry is now known, it is safer to describe the experiment by stating only the starting temperature avoiding the discussion of phenomena as they would happen at that temperature entirely.

Similar speculations will be replaced by exact measurements soon. During the research for this paper, a publication by Teather and Klassen (11) appeared on measurements of temperature changes during pulse radiolysis at 6 K. The authors used thermocouples made of 0.08 mm dia. teflon coated wires of chromel and gold containing 0.07 atomic % iron with a soldered junction. Glycerol glass had been the object of irradiation, being the only transparent material of known specific heat from 2 K onwards. Pulses of 35 MeV electrons of 40 ns or 1  $\mu$ s duration were used. The heat capacity of the thermocouple was very small compared to that of the glycerol sample. After the pulse a jump of temperature was observed. A part of the signal decays during the first 5 ms after the radiation pulse and a stable level persists for

about 0.5 s indicating the temperature of the sample. The temperature returns almost to its starting values in about 5 s. The initial 5 ms decay is related to processes within the thermocouple itself, perhaps thermal equilibration between the three components, Au-Fe, chromel and solder of the thermocouple junction. In one of the experiments, a 40 ns electron pulse delivered a dose of 6.1 krad, the temperature rise, measured 10 ms after the start of the transient was  $\Delta$  5.0 K, indicating a sample temperature of 11 K. The calculated temperature rise, assuming total conversion of the absorbed energy into heat was  $\Delta$  5.0 K, while the rise calculated assuming 20% chemical potential energy (unrecombined ions, electron trapped in glycerol, etc.) was  $\Delta$  4.8 °K. The close agreement between the calculated and the measured temperature rise in the case of glycerol, verified the accuracy of this measuring technique and allowed the use of the system to measure specific heats of other cold glasses investigated in radiation chemistry.

Considering processing at these low temperatures one has to remember that the heating from doses on the order of kilorads is already as high as from megarad doses at room temperature. Therefore application of low temperature radiation processing not only at helium temperatures but already at liquid nitrogen temperature and at high doses may be realized only by delivering single pulses. They have to be repeated with low frequency, resulting in a very low average dose rate, accompanied by a thermal quasi steady state (see Part 4). Such step irradiation is unavoidable because materials other than those mentioned above

(aqueous systems, glycerol, organic solvents, etc) have much lower heat capacity (especially semiconductors and metals).

The heat evolving during irradiation may be absorbed in some cases not only by the heat capacity, but also by the latent heat of phase change (melting or evaporation). These heats are by far higher than specific heats, but reaching these points in regular radiation processing is difficult to imagine. They may occur in the case of irregularities, e.g. of the breakdown of the conveyor or extremely exothermic, unexpected polymerization reactions. The only normal case of radiation heat being buffered by a phase change is probably the increased rate of evaporation of liquid nitrogen. This is a most obvious case, regularly encountered in low temperature processing. As the heat of evaporation of liquid nitrogen is  $47.5 \text{ cal g}^{-1}$ , one megarad causes 5.0 g out of every 100 g to evaporate (when irradiated at 77 K), in addition to the usual rate of evaporation determined by the quality of insulation and the outside temperature. In the case of ice (water), one megarad causes 3.0 g out of every 100 g ice (of  $0^\circ\text{C}$ ) to melt or 10.5 g at full sterilization with 3.5 Mrad, when irradiated at  $0^\circ\text{C}$ .

The temperature increase due to irradiation has safety implications. There have been cases of fire under the window of a high power accelerator, because an unusual slow down of the conveyor was accompanied by rapidly increasing dose and temperature of the target. Automatic safety systems which switch off the beam always work with some delay. That delay has to be known, and the dose absorbed before shut down by the particular

system has to be estimated. One has to consider then whether the ignition temperature will be reached. If a large, thick mass of dielectric is irradiated, electrical discharge of excess electrons is very probable. The resulting spark can ignite a hot irradiated object. Another immediate cause of ignition may be a piece of metal which is heated to much higher temperatures (Table 1).

All information in Part 3 referred to adiabatic conditions of irradiation such as those prevailing in accelerator irradiation. Let us discuss the increase of temperature in high activity gamma sources. The heat generated in such an irradiation mode is exactly the same as with electrons. The energetics explained in Part 2 also apply here, although the proportions of various forms of energy are different (Fig. 1, III and IV). The main difference is the dose rate which is so low in gamma irradiation that the deposition of heat competes with heat exchange between the irradiated object and the environment. Practically every object in the irradiation chamber attains a steady state temperature resulting from equilibrium between the heat generated by absorbed energy and the heat escaping to the surroundings. Constructors of the early Gammacell at the Atomic Energy of Canada Limited have noticed that the equilibrium temperature of a material placed in the irradiation chamber is a function of its density (Fig. 4). The equilibrium temperature, as every steady state, is very labile and is subject to the slightest change of isolation, air flow around the object, etc. Therefore the diagram cannot serve as a reference, but only as a guide. Even ones own experiments of a similar kind have limited applicability when

the shape of the object and other conditions of irradiation are slightly changed.

In high power gamma irradiation a new thermal factor appears, which was absent in accelerator irradiation. The starting temperature in accelerator irradiation is usually ambient, corresponding to the temperature of the ventilating air, or of the stream of nitrogen supplied in large volumes to prevent a negative influence of oxygen in some polymerizing systems. The thermal radiation of the accelerator window may be neglected if designers of the accelerator provided not only gas cooling but also water cooling around the window. In large gamma irradiation facilities, especially exceeding 1 mega Ci of cobalt 60  $> 37$  PBq), the cobalt 60 panel (rack) is itself a source of many kilowatts of heat emission. Already in laboratory sources like in the popular Gammacell 220 loaded to 6000 Ci and more, the irradiation chamber is always warm, changing the thermal environment and influencing the steady state temperature. Therefore some designers have introduced water cooling close to the Co-60 compartment (e.g. in the Soviet Issledovatyel). Large industrial gamma sources, usually stored in water pools are sufficiently cool while in the pool, but after lifting into the working position, placed in the center among travelling boxes, they act like multikilowatt electric heaters. Only an efficient exhaust system combined with injection of cool air may keep a reasonably steady temperature. Failure of ventilation and of transportation (movement) of boxes may lead to a fire, if the irradiated material has a low flame point. The nonadiabatic delivery of

energy in large gamma sources develops temperature problems, which cannot be neglected. Since calculations of temperature similar to those in accelerator irradiation are not possible, measurements must be performed. A test box, filled with a model material, to which a color temperature indicator has been applied is put into the irradiation train. The indicator has to be a permanent change type and not affected by ionizing radiation. A more precise measurement of the maximum temperature reached is very difficult, but hardly necessary.

#### 4. SOME CHOSEN ASPECTS OF THERMAL EFFECTS IN RADIATION PROCESSING

##### 4.1 Dosimetry

As it has been explained in Part 2 and 3, the thermal effects of irradiation are governed by strictly quantitative and highly precise relations, sometimes of a statistical precision better than chemical or physicochemical determinations of amount of products formed. Therefore calorimetry has been applied successfully as a dosimetric method early on in radio- and radiation chemistry. However, only metals do not show chemical changes under the irradiation, the temperature jumps favorably high, but the absorption characteristics of metals are badly matched to those of usually processed materials. The body of a calorimeter must be as close to the properties of the processed material as possible.

Calorimetric measurements on the chemical system under irradiation is precise enough to distinguish between the energy released as heat and that hidden as the change of internal energy. Therefore the calibration of the ferrous-ferric Fricke system could be

done and the G value established with high accuracy. Even when chemical changes are faint and seem to be neglected, calorimetry is precise enough to detect them. That is the case of the "pure" water dosimetric calorimeter, where distilled water is used as the energy absorbing medium. The water calorimeter has been used successfully for many years almost unchanged from its original form, developed at Risø National Laboratory in Denmark (12). It is specially designed for electrons from a linac ( $> 5$  MeV) and has shown accuracy of  $\pm 2\%$  sufficient for radiation processing and even for calibration of secondary dosimeter systems (e.g. PVC-film, hard, transparent, which are not better than  $\pm 7\%$  accurate themselves).

Only recently (14), Ross, Klassen and Smith, improving the precision of their calorimeter to  $\pm 0.3-0.5\%$  tried to investigate the role of gases dissolved in irradiated water. They found that saturation of water with a 50-50 hydrogen-oxygen mixture increased the exothermicity by  $2.1\%$  ( $+2.1\%$ ), saturation with oxygen reduced the exothermicity to  $-1.9\%$  (i.e.  $+1.9\%$  endothermicity) and saturation with nitrogen showed an exothermicity of  $-0.4-0.3\%$ . These values are very close to the ones calculated from the known mechanism of radiolysis of water which has since been computerized. The internal energy of irradiated aqueous solutions may be calculated at any stage and mode of irradiation (15-17). Commenting on these results one has to remark that filling routine calorimetric dosimeters with water saturated with nitrogen or argon seems to be advisable. Not only does it better secure recovery of the energy, not modified by chemical effects but it also diminishes the oxida-

tive action of the calorimeter medium on the walls of the vessel, usually made from polystyrene.

#### 4.2 Final temperature of composite objects.

The case of ideally homogeneous material as the object of radiation processing is limited to a few important cases, e.g. crosslinking polyethylene. A pigmented material is inhomogeneous from the point of view of energy deposition not to mention polyethylene with heavy atom compounds added to diminish flammability. The heterogeneous material being processed may be divided into several categories according to the geometric size, shape and distribution of phases, its percentage participation in the total volume of the sample, its energy absorption thermodynamics and its radiation chemistry. It is too early to discuss all three categories and their combinations in detail, therefore only a few illustrative examples will be given.

If a heavy constituent is incorporated into the material on the molecular level, consideration of heterogeneity of thermal response to irradiation is not needed. Nevertheless, the changed specific heat which is usually lowered must be applied in calculations.

Macroscopic heterogeneity, encountered with emulsions, suspensions and thin layer sandwiches demands careful analysis. For instance, Figure 4 shows a distribution of temperatures in accelerator irradiated natural latex for the purpose of crosslinking (18). About half of the sample has a much higher temperature with conventional reactions running several times quicker. There is no

convection in that thixotropic system and therefore thermal equilibration lasts almost a minute. Due to intolerably high differences in temperature, the processing of latex has to be divided into two irradiations, especially if modifying agents in the organic phase are volatile.

The most difficult situation occurs if comparatively thick metallic parts are incorporated, or are touching plastic material. Cases like this are not uncommon: insulated electrical cables, layers of plastic covering metallic sheets, medical devices containing parts made of inorganic polymers and metals. Let us assume that a medical device, made essentially from polypropylene, contains small Pyrex-type glass, aluminum and steel components. It has to obtain a dose of 3.0 Mrad from accelerated high energy electrons. Starting at 25°C, polypropylene will be heated up to 37°C, the other parts will be temporarily heated to much higher temperatures. Temperatures reached by glass, aluminum and steel from the dose of 3.0 Mrad will be respectively 50, 57 and 68°C. However, being in the place where the polypropylene is receiving 3.0 Mrad, they will absorb more than 3.0 Mrad because of their different energy absorption properties. Calculations show, that these maximum theoretical temperatures are respectively 113, 110 and 513°C! The real temporary temperature is in between the "3.0 Mrad" value and the maximum dose value. At lower energy of electrons the values are closer to the first set of temperatures. Radiation sterilization of medical supplies with accelerator irradiation is possible, in spite of this extreme local heating, because: a) the "low  $c_p$ -high  $d$ " components are made as thin as

possible, b) the low heat capacity does not mean only that the material is heated extensively from small amounts of energy; it means also that the cooling process is rapid and that the amount of energy delivered to the plastic is not a very high. c) All plastics have some tolerance for a short duration overheating.

After partial equilibration of temperature, the plastic surrounding the metal exhibits only a slightly elevated temperature in comparison to the plastic without metal. The metal absorbs more energy, resulting from the difference of electron densities between plastic and metal. This will also cause plastic below the metal to be shielded to some extent. The situation resembles the case of metallic thermocouple mentioned in part 3 (rise of temperature lasting for miliseconds). Nevertheless, during process development, interfaces between plastic and metal must be inspected and analysed for mechanical strength and possible chemical changes. In the case of doubt, measurement of real temperature as a function of time may be done, e.g. by inserting a thermocouple into the injection needle of a plastic syringe and irradiating the package with a straight, pulsed beam of electrons, without using a conveyor. Several doses of radiation higher than the envisioned process dose and subsequent observation of damage, may help.

#### 4.3 Measurement of the real temperature of an irradiated object

Measurement of the real temperature of a sample during irradiation has been already mentioned in previous parts of this paper for rather simple cases (single pulse irradiation of frozen samples (part 3) or temperature of composites in straight beam

irradiation (end of 4.2).

By far more complicated is a direct measurement under the scanning tube (horn) on/or above the conveyor belt, especially in the case of a low energy ( $< 1$  MeV), but high power accelerator. That case concerns usually the curing of thin layers of monomers compositions, usually covering a textile, paper, wood or metal substrate. Radiation induced polymerization generates heat, exceeding the physical heat even more than it is shown on Fig. 2 (inorganic chain reaction in aqueous system). The radiation processing is possible only because of minimal thickness of the coating and of forced, intensive cooling. In 1982, two mathematical approaches have been published, one in USA (20) another in the USSR (21) trying to calculate the temperatures in the irradiated object, moving under the window. As it can be expected, the temperature profiles gradients, both across the layer and along the surface in the direction of transportation are very complex ones and most sensitive to the rate of gas flow and thickness of the layer. Both Authors do not mention the possibility of cooling the bottom of the material, which will be mentioned in 4.4, as the case belonging to the irradiation at lower temperatures. Quoted Authors experience may be of help in development of new technologies, but the final answer may be obtained only in pilot plant type experiment. An important element of the experiment remains the measurement of temperature.

A sensing element always modifies the distribution of energy in the sample and alters heat transport properties of the target. These effects can be minimized only by miniaturization of the

temperature sensor with respect to depth of electrons' penetration, and its proportion to the target's mass and electron stopping power. Currently very small thermocouples and thermistors are available with active sensing volumes of the order of 0.07 cubic millimeters. It is useful to compare both sensors with respect to several aspects important to the contemplated measurement. The mechanical strength of thermocouple wire is greater than that of the nonmetallic substances of which thermistors are made. It is arguable that the least massive temperature sensors can be thermocouples especially when it is taken into account that even micro-miniature thermistors must be encased in some rigid medium like glass to provide mechanical integrity. Thermocouples generate a potential as a function of temperature and neither add nor subtract significant heat to their environment. Thermistors change their resistance as a function of temperature. To detect this, a potential must be applied across the thermistor. This causes selfheating, usually on the order of few microwatts, which must be accounted for, especially when low power (low dose) measurements are desired. This effect may be neglected at high powers such as those used in radiation processing, unless, of course the combined temperature rise due to irradiation and radiation induced reaction is great enough to increase the conductivity of the thermistor to the point where a virtual short circuit condition exists causing runaway selfheating in the thermistor. Therefore, due consideration must be given to the thermistor sensing circuit to prevent such a condition.

Both types of sensor can be expected to suffer some radiation

damage. The nonmetallic composition of thermistors may cause them to be more susceptible by virtue of possible radiation induced chemical reactions in the material. Detailed data on radiation damage of thermistors at high doses of low energy electrons is not available. Thermistors have been found satisfactory for use at the low doses encountered in space research and researchers in radiation processing indicate that significant changes in thermistor response have not been a problem. Radiation induced reaction can be hypothesized between the irradiated medium and the sensor material for both thermocouple wires and nonmetallic thermistor materials. It is advisable for the sensor to be enveloped by a thin coating of a high thermal conductivity, relatively inert material whose potential radiation induced reactions with either the sensor material or the irradiated target would be negligible. Every choice will have a compromising character. Fused quartz or glass are probably the best compromise since they are rather inert and despite their poor thermal conductivity should not severely impede heatflow to the sensor if they are applied as very thin coatings whose thickness is small compared to the cross section of the active volume of the sensor.

Both thermocouples and thermistors are built from different materials whose specific ionization characteristics are different. In a radiation field these materials will develop substantial differences of potentials. Especially in semiconducting materials the values may be high (19). Thermocouples will generate an additional EMF due to these ionizations. Thermistors are immune to this problem because the

potential difference between the thermistor material and either of the metal wire sensing connectors will be mutually compensated and will not contribute to conductivity change across the thermistor material.

Many of these considerations have been taken into account in the system under development at Johnson & Johnson Absorbent Technology (22) for measuring the rate of temperature rise of a reacting mixture during irradiation by a scanned beam of low energy electrons in real time. Discrete rapid temperature measurements are synchronized with the scan rate of the accelerator so that no measurements are being made concurrent with irradiation but rather immediately after each sweep of the beam. This eliminates specific ionization difference effects and noise induced in sensor connector leads, due to the magnetic and electric fields induced by the motion of the target and the scanning electron beam. The temperature measuring system lends itself to routine application on scanned accelerators rapidly yielding information about the thermal balance of radiation induced reactions, thus making the optimization of new applications easier.

Although thermocouples and thermistors are frequently used at present, they are <sup>not</sup> the only options. Degnan (20) has reported the application of a noncontacting piezoelectric infrared pyrometer in the measurement of the surface temperature of cured coating, ca 5 cm from the edge of the electron window. No characteristics of the sensor and no comparison between the IR sensor and medium contact devices were provided.

#### 4.4 Processing at temperatures other than ambient.

Radiation processing is essentially working at ambient temperatures, due to the ability of ionizing radiation to create reactive species not requiring external thermal energy. However, examples of temperature increase of irradiated systems show, that sometimes the increase of temperature may spoil all advantages which the radiation processing, as a "cold" method is creating. Therefore for that or some other reasons one has to start at lower temperatures to remove excess heat during or just after irradiation or to modify the result of irradiation by heating. These variants of irradiation are connected with the rate of chemical reactions involved, which are influenced by the temperature. Perhaps the best way to explain the meaning of the temperature coefficient and thus of activation energy is to do it on the example of applied photochemistry i.e. photography, which is not far, in principle from the radiation processing and at the same time is very close to everyday experience. As everybody knows, there is no correction introduced whether the picture is taken at arctic or equatorial conditions. The amount of light supplied to the film counts and has to be adjusted to the sensitivity of the film only. This is due to the negligible value of the temperature coefficient (almost zero activation energy) of the primary event in the silver halide crystal, an act similar to the primary effect in interactions with ionizing radiation. However what happens next in the photographic process is temperature dependent. Already the storage of the latent picture is influenced by the temperature, that's why refrigerated storage of exposed film is advised as well as prompt

developing. A really high activation energy is involved in the development, as one knows from the Polaroid process. Some color processing techniques procedures demand a control of temperature down to within  $\Delta 1$  K!

Keeping in mind the photographic experience we may expect that all simple reactions induced by ionizing radiation will proceed without activation energy, and without influence of temperature. Usually that is true for low radiation yields not exceeding few units of G. In that case the primary reactions will proceed almost independently of the starting temperature of irradiation ("photographic film exposure"). That is no longer the case with secondary reactions which sometimes proceed with enormous temperature coefficients ("developing of photographic film"). Often, at low temperature the primary products are frozen and do not react, but after heating they start to react explosively.

Therefore the production of heat shrinkable olefins is principally a room temperature operation and only sometimes demands a double step irradiation (total dose administered in two portions) with cooling down in between runs under the accelerator. Other cases may demand a more complicated approach, e.g. sterilization of human bones for transplants. That operation must be done at cryogenic conditions, but still an ordinary conveyor may be used (23). The material is stored before and after the sterilization under liquid nitrogen (bank of bones) and temporary warming up during the irradiation and connected manipulations to ca  $-100^{\circ}\text{C}$  (effect of radiation on the sample and packing material) is not important. In many cases, however, the unit operation of irradiation (24) must be

substituted by a dedicated device. That happens, e.g. in the case of covering paper with polymers. A band of paper is coated with monomer and is moving on a cooled transfer drum under the window of an accelerator. Because the drum is of rather large diameter, the object is sufficiently cooled before reaching the beam and stays for the same time on the cool surface after the irradiation, to release excess heat. The scheme of such an irradiation can be found in Nablo's paper (25).

If it is necessary to irradiate at other temperatures than ambient, the influence of starting temperature on the process should be investigated. Experiments at precisely controlled temperatures are not easy and demand construction of special device (e.g. 26). High energy electrons makes the task comparatively easy but with low energy accelerators the experiments must be sometimes done on the industrial irradiation stand itself.

Finally, it is sometimes necessary to apply a very high dose (e.g. experiments with deep dehydrogenation, with radiation resistant polymers, or on many inorganic materials etc.). It can easily be done in gamma sources, without excessive rise of temperature, but because of low dose rates exposures are long. If such a time span is inconvenient, one can irradiate with the straight beam from an accelerator. In the authors laboratory the object is placed a rotating table. In the center a suitable semiquantitative temperature measuring device is placed e.g. thermocolor covered piece of processed material. Heat is taken from the sample by a stream of cold air, and the rotation secures a uniform distribution of heat and dose. After few minutes a steady

state is established similar to the one observed in gamma sources (c.f. Fig. 4), but at a much higher dose. As the relations governing the flow of heat are very complicated, the maximum rate of pulsing allowed not to exceed the desired temperature is adjusted by trial and error. Any further changes are matched to the cooling ability of the system. After adjusting the conditions and checking the temperature by more precise measurement, the two parameters - dose rate and cooling must be kept constant. In the case of radiation resistant inorganic hydrates based on silicates (27) it has been possible to apply hundreds of megarads per second. The cooling system must be reliable, otherwise the sample is destroyed very quickly, because the radiation energy deposited locally is comparable to that of a part of a nuclear weapon radiation spectrum (with respect to thermal effects only).

If the irradiated sample has to be kept without access to air, it must be sealed under a neutral gas, allowing it to increase its pressure when heated, but not under vacuum. The conditions of heat transport, already poor with gas insulation, are even worse under vacuum and are difficult to control.

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## CAPTIONS

Fig. 1. Energy balance in the initial step of delivery of radiative energy to the object. (Schematically, precise participation depends on a number of properties of particular radiation and the object): R - reflection, S - secondary penetrative radiation emitted from the inside of the object, A - part of energy absorbed, P - energy passing through.

- I. Light falling on the object which is opaque to the incident radiation.
- II. As I but object semitransparent. Also a transparent matrix containing species absorbing selectively.
- III. Ionizing quanta incident on a thick object.
- IV. As III but a thin object.
- V. Accelerated electrons of low energy; thickness of the object larger than the range.
- VI. Accelerated electrons, high energy, thickness of material adjusted to obtain homogeneity of dose.

Fig. 2. Energy balance of absorbed radiation energy, assumed initially as 100 and modified by chemical reaction, eventually released as heat.

Fig. 3 Change of specific heat of polystyrene with temperature. Shaded areas indicate the amount of heat supplied by 1 Mrad of radiation. Temperatures indicated by arrows show the calculated temperatures reached if the change

of  $c_p$  is taken into accounts (lower values) or is not (higher values).

Fig. 4. Temperature at the steady state for some materials filling the irradiation chamber of cobalt 60 (16 kCi) gamma source, Gammacell 220 by AECL. (Modified from the instruction book).

Fig. 5. Distribution of temperatures in the natural rubber latex, immediately after the high power accelerator irradiation to the dose of 10 Mrad. O - organic phase, A - aqueous phase. a) before, b) after the irradiation.

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Table 1

Example of Specific Heats ( $c_p$ ) and the Temperature Rise after Absorption of the Dose of 1 or 3 Mrads (10 or 30 kGy).

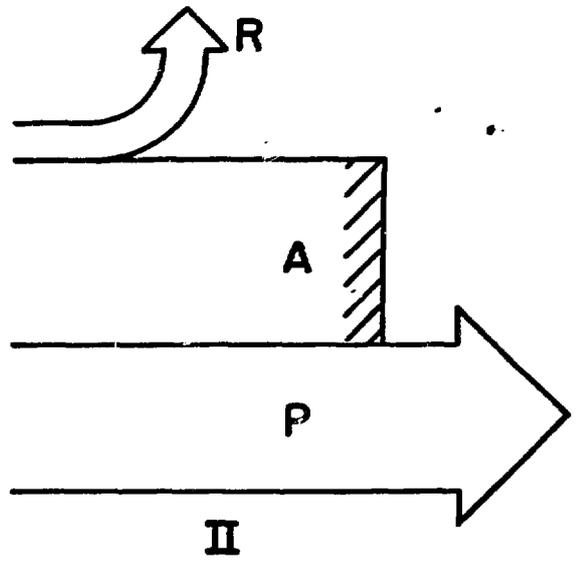
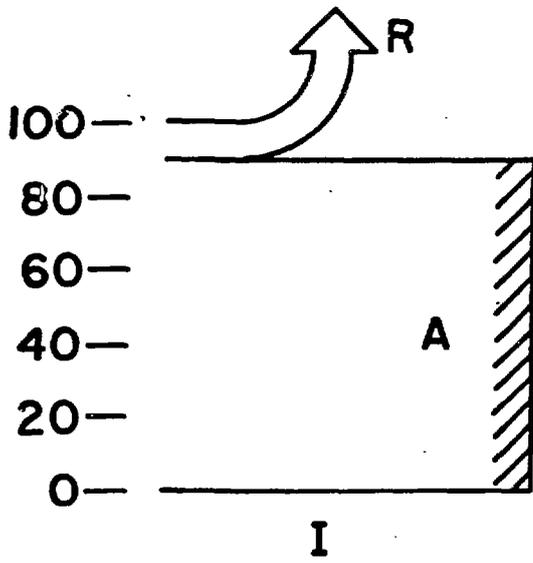
Material	specific heat at temperature		increase of the temperature after	
	C or K	cal/g K	1Mrad $\Delta$ K	3Mrad $\Delta$ K
water, liquid	21°C	0.998	2.39	7.17
water, ice	-21°C	0.467	5.06	14.9
water, ice	77 K	0.165	13.5	36.6
ammonia, solid	150 K	0.547	4.30	12.5
ammonia, solid	77 K	0.262	8.57	23.3
acetone, liquid	25°C	0.528	4.4	
aniline, liquid	25°C	0.741	3.2	
benzene, liquid	25°C	0.406	5.8	
chloroform, liquid	25°C	0.225	10.4	
di-ethylether, liquid	25°C	0.547	4.3	
ethanol, liquid	25°C	0.581	4.1	
octane, liquid	25°C	0.578	4.0	
poly acrylo nitrile	25°C	0.308	7.63	22.4
poly acrylo nitrile	77 K	0.108	19.8	52.6
polyamide (Nylon 6)	25°C	0.356	6.57	19.4
polyamide (Nylon 6)	77 K	0.115	18.8	50.1
polycarbonate, amorphous	25°C	0.287	8.23	24.0
polycarbonate, amorphous	77 K	0.0834	25.4	63.9
polyethylene, amorphous	25°C	0.524	4.53	13.5
polyethylene, amorphous	77 K	0.134	16.4	43.5
polyethylene, crystalline	25°C	0.370	6.42	18.9
polyethylene, crystalline	77 K	0.128	17.0	40.8
polymethylmethacrylate, am.	25°C	0.327	7.22	21.2
polymethylmethacrylate, am.	77 K	0.108	19.1	51.8
polypropylene, amorphous	25°C	0.500	4.76	12.0
polypropylene, amorphous	77 K	0.129	16.9	41.7
polystyrene, amorphous	25°C	0.290	8.11	23.6
polystyrene, amorphous	77 K	0.0896	23.9	62.3
poly(vinyl chloride), am.	25°C	0.226	10.4	30.3
poly(vinyl chloride), am.	77 K	0.0858	16.4	66.3
carbon (graphite)	25°C	0.172	13.5	38.5
silicon, crystalline	25°C	0.171	13.6	40
silicon, crystalline	77 K	0.0424	40	89
iron, $\alpha$	25°C	0.107	15.5	43
iron, $\alpha$	77 K	0.0344	46	107
aluminum	25°C	0.210	10.6	32.6
aluminum	77 K	0.0803	24.2	57.8
Al <sub>2</sub> O <sub>3</sub> , NBS standard	25°C	0.185	12.7	37.0
Al <sub>2</sub> O <sub>3</sub> , NBS standard	77 K	0.0153	62.2	117
copper	25°C	0.0920	25.7	76.8
copper	77 K	0.0470	40.8	105
silver	25°C	0.056	42	126
silver	77 K	0.0385	54	140

Table 1 (continued)

platinum	25°C	0.0326	70	
platinum	77 K	0.0204	90	
lead	25°C	0.031	74	216
lead	77 K	0.027	86	245
mercury	25°C	0.0332	72	221

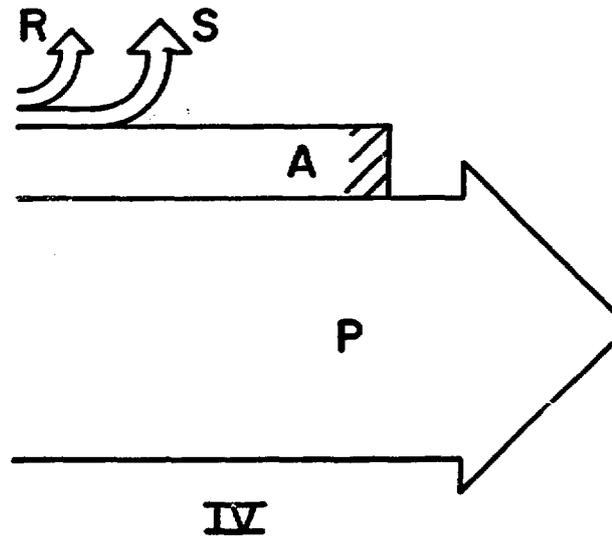
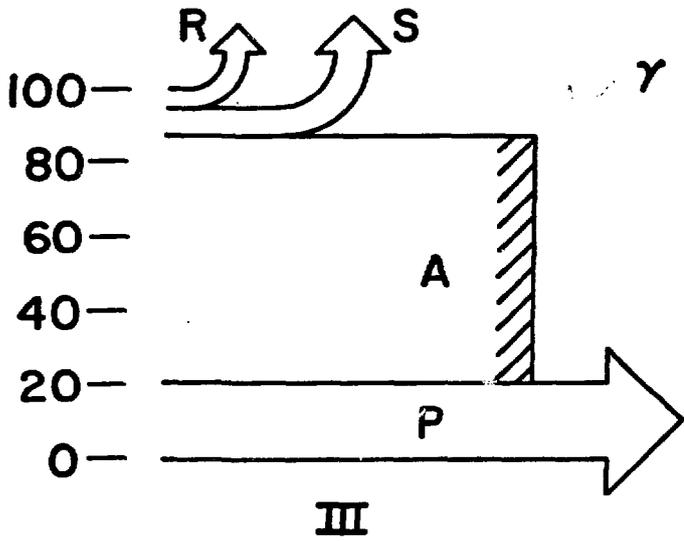
Two-digit value of the temperature increase means that not sufficiently accurate basic data are available. All temperatures are calculated with consideration of  $c_p = f(T)$ . Values of temperature increase are not corrected for a change of energy due to a chemical reaction, if any.

IR-VIS-UV:



IONIZING:

$\gamma$



IONIZING:

$e^-$

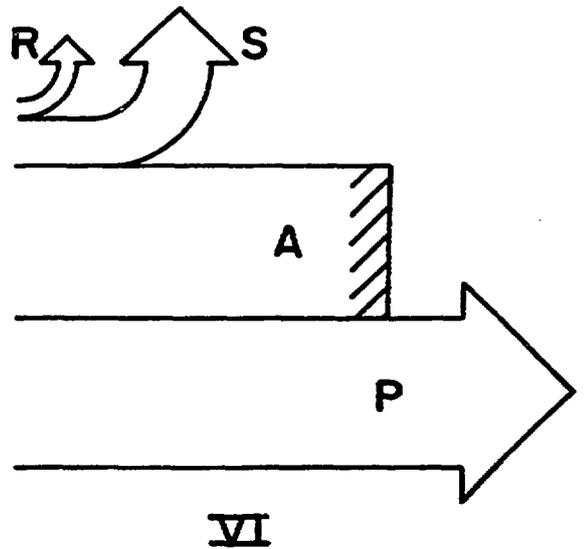
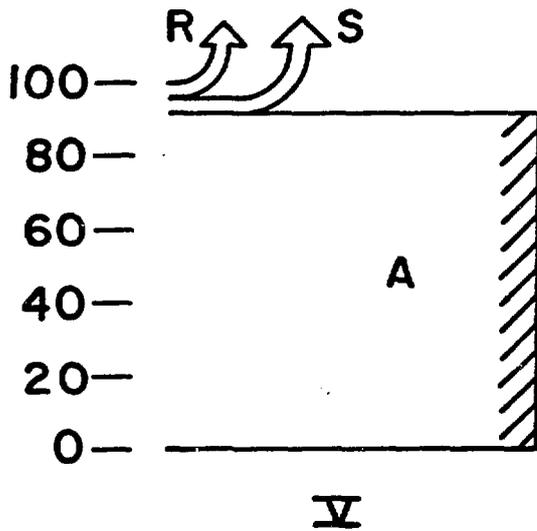
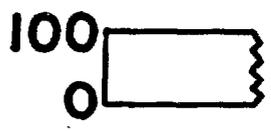


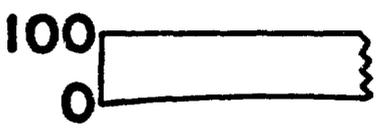
FIG.1



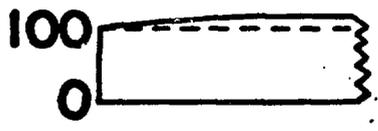
**METALS**



**WATER**



**Fe<sup>2+</sup>, H<sub>2</sub>SO<sub>4</sub> deaerated**



**Fe<sup>2+</sup>, O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>**

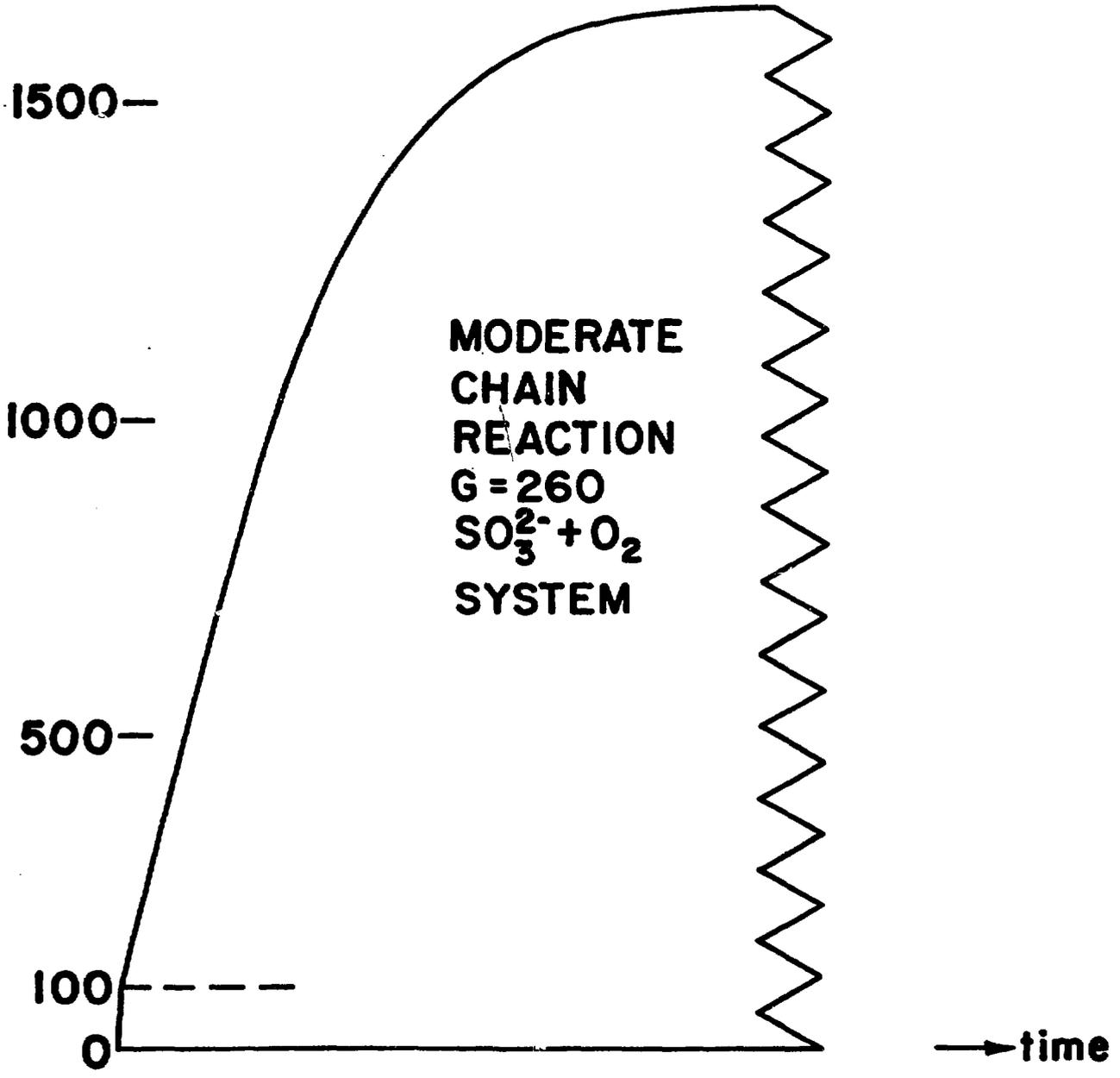


FIG. 2

cal/g K

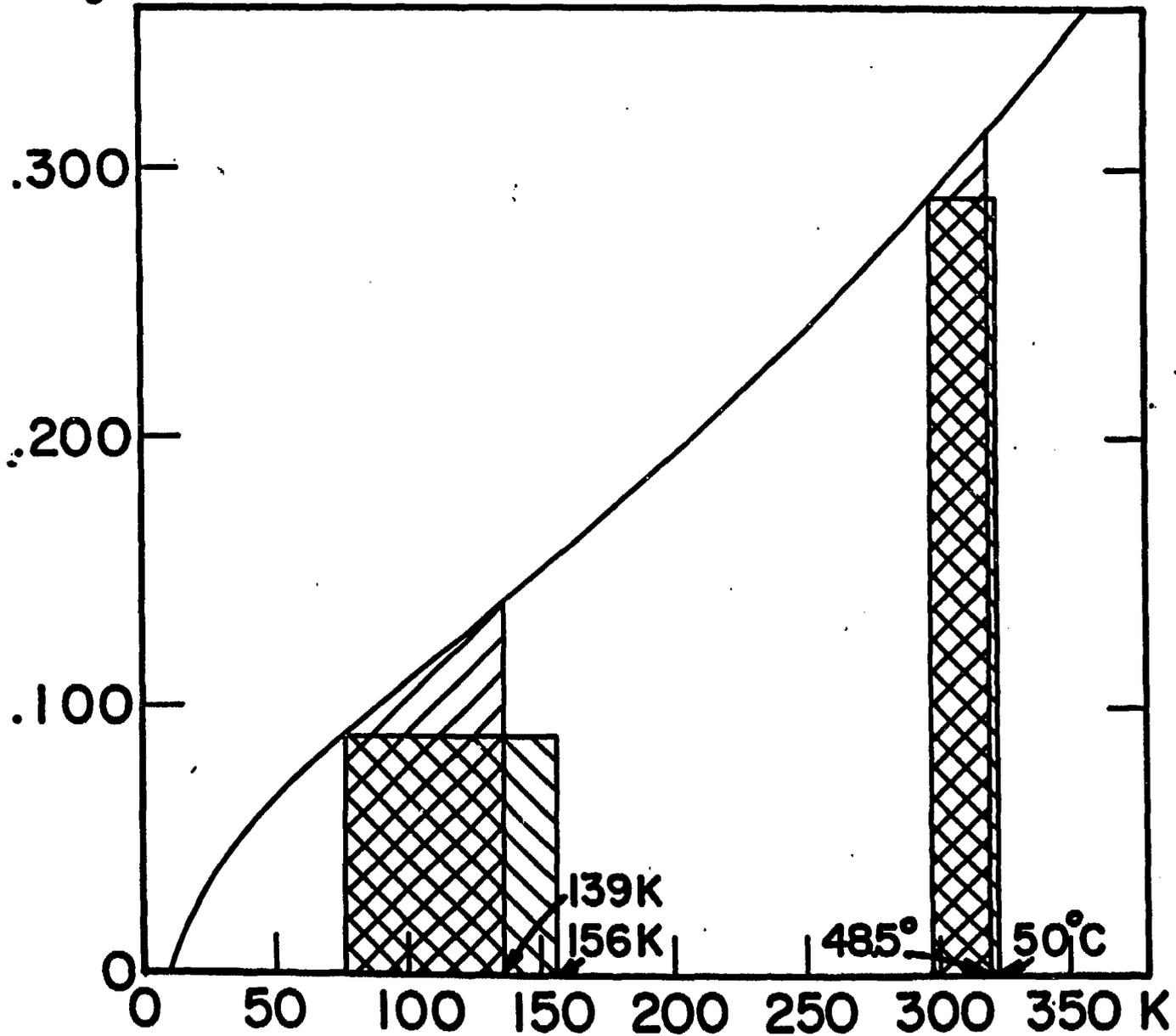


Fig. 3

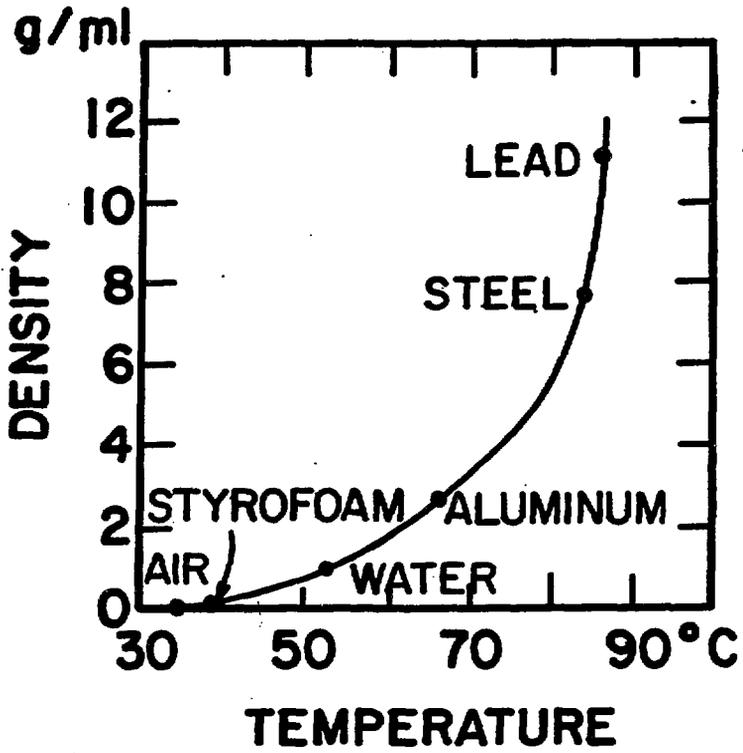


Fig. 4

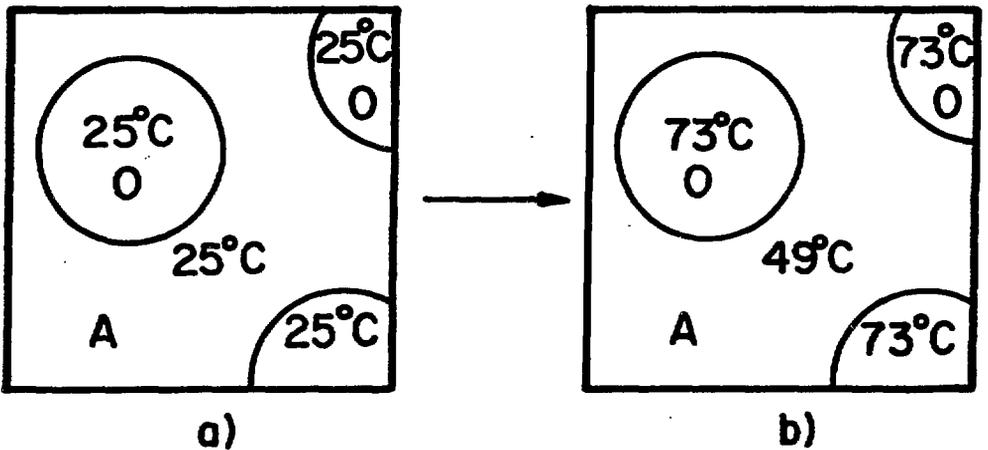


Fig. 5